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Contents

Chapter - 1

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Chapter - 1

Plant Mediated Synthesis of Zinc Oxide Nanoparticles using Acalypha Fruticosa Forssk Combined with Curcumin with Special Reference to Antibacterial and Anticancer

Sagar I. Shinde, Santosh R. Kshirsagar and Sandip P. Gondake

Abstract

The use of medicinal plant extract in the manufacture of metal oxide nanoparticles is a viable alternative to the traditional chemical technique. This study used a green technique to synthesis zinc oxide nanoparticles from Acalypha fruticosa forssk leaf extract, which is an endemic medicinal plant growing in home gardens across India. UV-DRS, FTIR, SEM with EDAX, and IR are some of the techniques used. The antibacterial efficacy of the produced ZnO nanoparticles was further tested against clinical and standard strains of E. coli, S. aureus, and P. aeruginosa.

Keywords: Acalypha fruticosa forssk, ZnO, nano particle, antibacterial, plant

Introduction

Biosynthesis of metal nanoparticles is one of the most modern and dynamically active in the field of pharmaceutical science which is simplest and ecofriendly method due to have safer and cost-effective alternative to other chemical and physical methods [1, 2]. Natural plant extracts are promising for the production of metal nanoparticles due to possessing secondary metabolites as reducing agents as well as stabilizing agents [3]. The natural plants are easily available and offer simplicity. Generally, plant extract contains number of antioxidants which includes polyphenols, proteins, carbohydrates, amino acids etc. which can reduce the metal ions to metal salt solution [4] which can lead to the formation of nanoparticles. Biosynthesis of different metal oxide nanoparticles were carried out by using many plant extracts which includes *Hordeum vulgare, Rumex Acetosa, Caesalpinia bonducella, Nerium oleander* etc. [5-7]. Metal oxide nanoparticles like CuO, MgO, NiO, TiO_2 etc. were prepare by using natural origin to explore the superior biological activities [8-10]. ZnO is one of the essential semiconducting materials which has unique advantageous such ultraviolet resistant property, remarkable catalytic activity, high surface area and biocompatible [11-12]. In addition, greener synthesis of ZnO nanoparticles has attracted in the field of biomedical application which is simplest and ecofriendly method [13]. The synthesized ZnO nanoparticles are found to have various therapeutic uses like antioxidant, anti-inflammatory, antifungal, antidiabetic etc. [14] which were synthesized by using only single plant origins. However, they are not effective due to have lower biological activities. The combination of plant extract for the production of nanoparticles has attracted distinct advantages offering improve or synergetic biological activities [15]. This work is mooted out to synthesis the metal oxide nanoparticles using two natural sources such as *Acalypha fruticosa Forssk* and curcumin. Both plants are freely available and contain numerous bioactive ingredients such as vitamins, minerals, enzymes, polysaccharides, phenolic compounds and organic acids [16,17]. The plants have traditionally chemotherapeutic agents due to produce the lower size particles. Green synthesis of metal oxides nanoparticles using *Acalypha fruticosa Forssk* plant extract and its antibacterial activity was reported [18-20]. Some of the works have been reported on the synthesis of metal oxide nanoparticles using curcumin which was tested for antibacterial activity against different pathogens [21, 22].

In this study, ZnO nanoparticles were synthesized by using two plant extracts such as *Acalypha fruticosa Forssk* and curcumin. The synthesized nanoparticles were evaluated by using different analytical techniques such as UV-DRS, FTIR, XRD, SEM with EDAX and TEM. Antibacterial and anticancer activities were also investigated.

Materials and methods

Synthesis of ZnO Nps

$ZnSO_4 \cdot 7H_2O$ (0.4 M) and NaOH (0.8 M) were dis- solved in distilled water. Co-precipitation of ZnO nanoparticles was achieved by adding NaOH dropwise to ZnSO4 7H2O with steady stirring at 80 °C until a white precipitate appeared. The precipitate was washed multiple times with deionized water, then ethanol, before being dried in a hot air oven for 5 hours at 80°C. To obtain nano-sized ZnO, the dried samples were calcined at 350 °C for 3 hours.

Characterization methods

A JASCO V-550 twin beam spectrophotometer with PMT detector was used to measure Ultra Violet-Visible-Diffuse reflectance spectroscopy (UV-Vis-DRS). The samples were placed in a quart's cuvette with a 1 cm light-path length, and the light absorption spectra were calculated using deionized water as a reference. A Fourier Transform Infrared (FT-IR) spectrophotometer was used to determine the surface structure (JASCO-RT-IR-460 plus). The JSM-6701F-6701 device was used to take SEM pictures in both back scattered electron and forward scattered electron modes. An energy dispersive X-ray spectroscopy (EDX) linked to the SEM detected the elemental analysis.

Antimicrobial activity

The synthesized ZnO was tested for antibacterial and antifungal properties. ZnO was investigated for antibacterial activity against three bacterial strains: E. coli, S. aureus, and P. aeruginosa. The samples were dissolved in dimethyl sulphoxide, which was then concentrated to the appropriate levels. By employing the well diffusion method, the bacterial and fungal strains were inoculated separately in 30 mL of nutrient broth in a conical flask and incubated for 24 hours to obtain active strain. Separate petri dishes were filled with Muller Hinton agar. After solidification, 0.25 mL of test strains were inoculated separately in the media, with special attention paid to homogenization. The experiment was carried out in an aseptic environment. After the material had solidified, a sterile borer was used to make a well in the plates (5mm). The test sample (40 L) was poured into the well, and the plates were incubated at 37 °C for 72 hours. Triplicates of each sample were tested. The diameter of the zone of inhibition was used to determine microbial growth.

Results and discussion

FT-IR analysis

FTIR spectroscopy was used to evaluate the presence of functional groups present in the synthesized samples. The FTIR spectra of pure and *Acalypha fruticosa Forssk* assisted zinc oxide samples are shown in Fig.1. The absorption peak at 642 cm^{-1} is the characteristic stretching vibration of ZnO originating from the Zn and O bond [23]. The peak at 1630 cm^{-1} is due to the OH group which is ascribed to water molecules [24]. In addition to that, Broad peaks at 693.45 cm^{-1}, 964.54 cm^{-1}, 1062.37 cm^{-1}, 1411.89 cm^{-1}, 1442.75 cm^{-1}, 1562.34 cm^{-1}, indicated the presence of the hydroxyl group, an aromatic group, amine group, saturated primary alcohol. The spectra showed a broad band around at 3450 cm^{-1} which is due to the stretching vibration primary amine. Also, the sharp peak at 2695 cm^{-1} is related to O-H stretching vibrations [25]. The overall observation proves the existence of phenolic compounds, terpenoids or proteins that bound to the surface of ZnO nanoparticles which may have contributed from the *Acalypha fruticosa Forssk* plant extract and curcumin. More over the proteins present in the medium might also prevent the agglomeration and aids stabilization on forming a cover on the metal nanoparticles. The metal oxygen frequencies observed for the respective metal oxide is in accordance with literature values. The results obtained from FT IR studies indicate that the phenolic compounds, flavonoids, and other biological molecules present in the plant extract and curcumin can trigger the reduction of zinc salt and control the size of synthesized Nps [3].

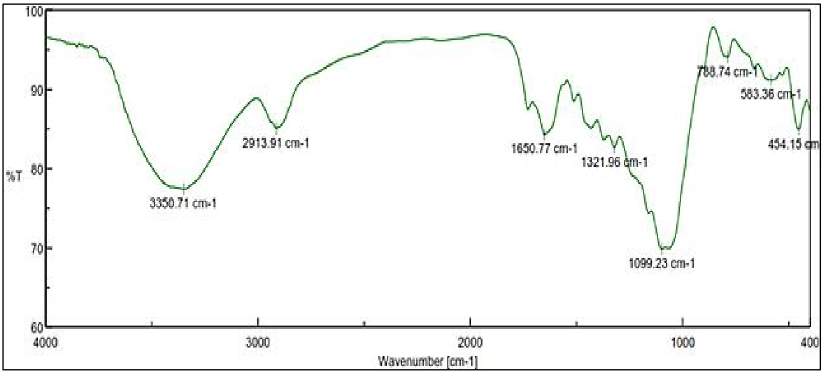

Fig 1: FT-IR spectrum of ZnO/*Acalypha fruticosa Forssk* nanoparticles.

Diffused reflectance spectroscopy

The absorption spectrum of pure ZnO, ZnO/*Acalypha fruticosa Forssk* and ZnO/*Acalypha fruticosa Forssk/curcumin* nanoparticles were shown in Fig. 2 which was evaluated by the UV-Vis spectroscopy to find the optical properties of zinc oxide nanoparticles. Pure ZnO and *Acalypha fruticosa Forssk* assisted ZnO nanoparticles showed a characteristic absorption bands at 359 nm and 352 nm respectively [26]. The ZnO/*Acalypha fruticosa Forssk*/curcumin showed a band at 350 nm. It is observed that the *Acalypha fruticosa Forssk* assisted ZnO nanoparticles which are having blue shift compared to the pure ZnO. This may be attributed to the quantum size effect and suggests that the addition of *Acalypha fruticosa Forssk* significantly affects the particle size and therefore the absorbance properties have been changed. On the other hand, sample without *Acalypha fruticosa Forssk* and curcumin shows a red shift of the UV-Visible absorption which can be attributed to the larger particle size. The optical absorption spectra of noble metal nanoparticles are known to exhibit unique optical properties due to the property of Surface Plasmon Resonance (SPR), which shift to longer wavelengths with increasing particle size [27].

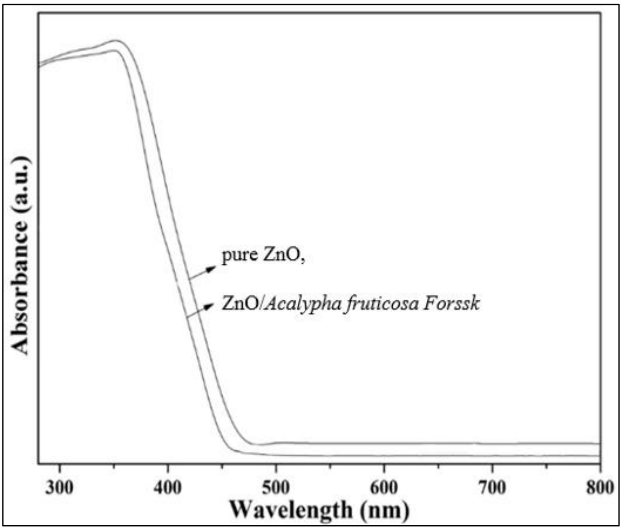

Fig 2: Diffuse reflectance spectra of pure ZnO, ZnO/*Acalypha fruticosa Forssk* and ZnO/*Acalypha fruticosa Forssk*/curcumin nanoparticle

SEM with EDX analysis

SEM with EDX results was employed to explore the surface morphology and metal present in the synthesized samples. Fig.3 shows the surface morphology of pure ZnO, ZnO/*Acalypha fruticosa Forssk* which was investigated by SEM analysis with X55,000 magnification. Image a clearly showed flower-like morphology whereas in Fig. 4b and 4c revealed sheet-like morphology. There was no agglomeration observed due to protein present in the *Acalypha fruticosa Forssk* as a stabilizing agent around which can prevent the particles formed from aggregating and making them more dispersible by acting as a bio template [29]. Meanwhile the morphology sizes of the all samples were different and confirmed the average sizes about 100 nm.

The surface of the ZnO/*Acalypha fruticosa Forssk* has slightly rougher than that of the pure ZnO, which might be due to the void between the particles. In addition to that, it seen that sheet-like structures were made up of many tiny ZnO nanoparticles in Fig. 3 The SEM results clearly indicated that the *Acalypha fruticosa Forssk* and have an impact on the morphology and particle size of zinc oxide. Fig.4d shown the energy dispersive X-ray analysis (EDAX) spectrum of *Acalypha fruticosa Forssk* and assisted ZnO sample. The expected stoichiometric mass percent of zinc and oxygen is 72.96% and 27.04% respectively. The EDX results revealed that the samples were mainly composed of Zn and O only without any other impurity, and were in good agreement with the XRD analysis [30]. The weak signals in EDX spectra may be due to the presence of macromolecules such as alkaloids, flavonoids and phenolic compounds in *Acalypha fruticosa Forssk* extract [31].

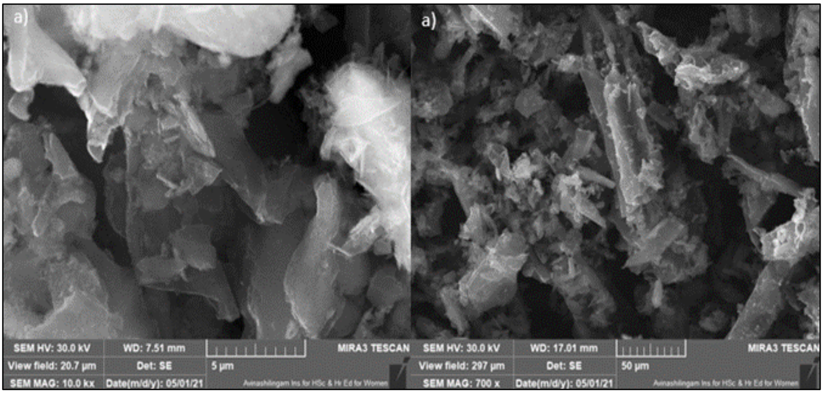

Fig 3: SEM images of Pure a) ZnO and b) ZnO/*Acalypha fruticosa Forssk* nanoparticles

Antibacterial activity

The antibacterial activities of pure ZnO, ZnO/*Acalypha fruticosa Forssk* and ZnO/*Acalypha fruticosa Forssk/*curcumin nanoparticles were tested against five bacterial strains such as, *S. Aeureus, M. luteus, P. vulgaris, E. coli* and *P. aeruginosa* at various concentrations such as 10 µg/mL, 20 µg/mL, 30 µg/mL, and 40 µg/mL as shown in Fig. 6(A-C). The results for all the samples are represented in tables (1-3). The analysis was carried out using positive control Chloramphenicol as standard. The maximum zone of inhibition (13 ± 0.31 mm) of ZnO is absorbed against *E. coli* and minimum zone of inhibition (9 ± 0.15 mm) is observed against *S. Aureus*. The size of the inhibitory zones varies with type of pathogens and the concentration of the samples. The maximum antibacterial activity (15 ± 0.85 mm) of ZnO/*Acalypha fruticosa Forssk* is absorbed against *E. coli* and minimum activity (13 ± 0.15mm) is observed against S. *aureus*. The antibacterial activity has increased for increasing sample concentration of 40 µl. The maximum zone of inhibition (17 ± 0.18 mm) is obtained for ZnO/*Acalypha fruticosa Forssk*/cur nanoparticles against *E. coli* and minimum activity is obtained (15 ± 0.07 mm) against S. *aureus* (Fig. 4). The observed value of inhibition is in good agreement with earlier studies [33].

From the observations it is seen that *E. coli* is highly sensitive to ZnO nanoparticles due to its high lipopolysachride and thick peptide glycane. The antibacterial activity of ZnO/*Acalypha fruticosa Forssk* nanoparticles has been originate to be due to a reaction of the ZnO surface with water and production of elevated levels of reactive oxygen species, namely hydroxyl radicals and in turn induces oxidative pressure. Correspondingly, an exposure of bacteria to the small ZnO nanoparticles resulted in an increased cellular internalization of the nanoparticles and the bacterial cell damage [34]. The enhanced activity is attained for ZnO/*Acalypha fruticosa Forssk* nanoparticles due to the strong attack on the surface of the cell wall and slowly penetrated into the inside cell consequently kill the bacteria. Since the ZnO/*Acalypha fruticosa Forssk* nanoparticles has smaller particles size (22.4 nm) thus made it easy to penetrate the cell wall. The less effect against of *S. aureus* due to the presence of thick layers of peptidoglycans present on the cell membrane [35].

The zinc oxide nanoparticles apprehended antibacterial activity that the surface of nanoparticle could easily form a layer of water, thus zinc oxide could be released into the water. The main composition of bacteria cell-membrane phospholipid bilayers and the protein molecules and the phosphate in phospholipid molecules owned negative electricity, the entire cell membrane to be negatively charged. Therefore, the zinc oxide with positive electricity were able to bind to bacteria cell-membrane quickly, which led the structures of bacteria to be changed and damaged. Furthermore, the antibacterial activity of the zinc oxide nanoparticles mostly appeared on the surface bind with the thiol (-SH) groups of protein present in the cell wall. This interaction decreases the cell permeability which leads to cell lyses [36-38].

From the above observations, it can be concluded that the smaller size of the biosynthesized nanoparticles has more efficient bactericidal activity than that synthesized by chemical method. The cell wall structures of Gram (−ve) and Gram (+ve) bacteria are different, which is responsible for toxicity. In the case of Gram (−ve) bacteria, the cell membrane is easily broken as the peptidoglycan layer is thinner, but the Gram (+ve) bacteria have thick peptidoglycan layer and hence, toxicity towards Gram (+ve) cell is significantly less [39]. The presence of flavonoids, phenolic compounds, and tannins noticed in the present study are responsible for enhanced antibacterial activity of biosynthesized ZnO nanoparticles than that synthesized by chemical method, by cell membrane lysis, inhibition of protein synthesis, proteolytic enzymes, and microbial adhesions [40].

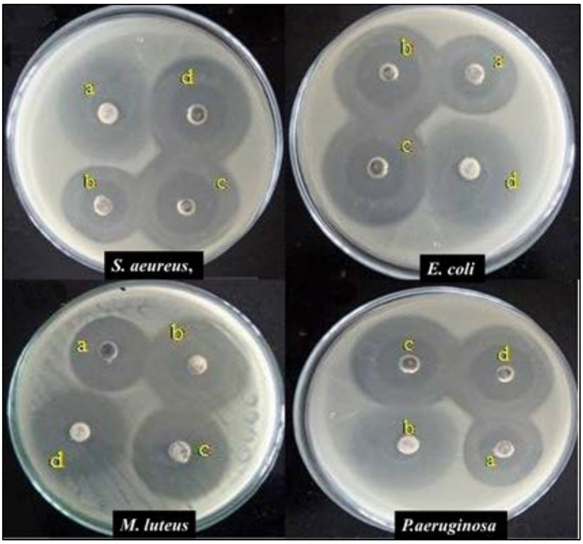

Fig 4: (B) Antibacterial activity of (a) ZnO (b) ZnO/*Acalypha fruticosa Forssk* (c) ZnO/*Acalypha fruticosa Forssk/curcumin* and (d) control against Gram (–ve) bacterial strains

Conclusion

Zinc oxide nanoparticles were successfully synthesized by greener method using *Acalypha fruticosa Forssk* and curcumin plant extracts and the formation of zinc oxide nanoparticles are confirmed by XRD, FTIR, UV-vis, SEM with EDX. The 30 µg/mL of curcumin loaded *Acalypha fruticosa Forssk* assisted ZnO nanoparticles showed superior antibacterial activity against two pathogens such as, *E. coli* and *P. aeruginosa*. This suggests that the ZnO/ *Acalypha fruticosa Forssk*/ sample can be used as an effective commercial antibacterial agent for the detection and destruction of bacterial strains**.**

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Chapter - 2

Sampling and Determination of PH using PH Meter

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Chapter - 2

Sampling and Determination of PH using PH Meter

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Abstract

Definition: pH is defined a minus the decimal logarithm of the hydrogen ion activity in a solution by virtue of its logarithmic nature pH is dimensionless quantity.

One of the most enlightening attributes of soil is its pH. Whether a soil is acidic, or basic has much to do with the solubility of various component, the relative bonding of ions on exchange sites, and activity of various micro-organisms. The plant nutrient availability is influenced by soil pH. The ideal pH range for availability of nutrients is 6.5to 7.5. Thomas (1957) noted that the three soil pH ranges are particularly informative: a pH less than 4 indicates the presence of free acids generally from association of sulphides, a pH below 5.5 suggests the likely occurrence of exchangeable Al and a pH from 7.8 to 8.2 indicates presence of $caCO_3$. In this chapter we have done the sampling of soil and determine PH of the soil by PH meter.

Keywords: pH meter, pH, soil sampling

Introduction

Agriculture is the primary source of livelihood for about 58% of India’s population. Collection of a good representative soil sample is the first criterion for a reliable soil test value. The analytical results are expected to be representative for the entire field. The basic principle for the soil sampling is that a field can be sampled in such a way that chemical analysis of collected soil samples will accurately reflect the field in respect of true nutrient status. Soil sampling is the process of taking a small sample of soil, which is then sent to a lab to determine the nutrient content. The analysis of the soil is carried out by taking samples of the soil and performing laboratory tests, which is then followed by an interpretation of the results. A soil test can determine fertility or the expected growth potential of the soil which indicates nutrient deficiencies, potential toxicities from excessive fertility and inhibitions from the presence of non-essential trace minerals. The test is used to mimic the function of roots to assimilate minerals.

Procedure for soil sampling

Take soil from 10 to 15 different places in the field, lawn or garden. Sample to a depth of 6 inches. Remove plant residue from the surface and use a spade, soil auger or soil sampling tube as illustrated. Place the soil in a clean bucket or container, mix thoroughly and take approximately 1 pint to send to the lab. The collected soil samples are analysed for different aspects. Out of that in this chapter we determine the P^H of the soil by using ^{PH}meter.

Some terms commonly associated with certain ranges in soil pH are

- **Extremely acid:** < than 4.5; lemon=2.5; vinegar=3.0; stomach acid=2.0; soda=2-4.
- **Very strongly acid:** 4.5-5.0; beer=4.5–5.0; tomatoes=4.5.
- **Strongly acid:** 5.1-5.5; carrots=5.0; asparagus=5.5; boric acid=5.2; cabbage=5.3.
- **Moderately acid:** 5.6-6.0; potatoes=5.6.
- **Slightly acid:** 6.1-6.5; salmon=6.2; cow's milk=6.5.
- **Neutral:** 6.6–7.3; saliva=6.6-7.3; blood=7.3; shrimp=7.0.
- **Slightly alkaline:** 7.4-7.8; eggs=7.6-7.8.
- **Moderately alkaline:** 7.9-8.4; sea water=8.2; sodium bicarbonate=8.4.
- **Strongly alkaline:** 8.5-9.0; borax=9.0.
- **Very strongly alkaline:** > than 9.1; milk of magnesia=10.5, ammonia=11.1; lime=12.

Natural soil pH depends on the rock from which the soil is formed. (parent material) and the weathering processes that acted on it for example climate, vegetation, topography and time. These processes tend to cause a lowering of pH (increase in acidity) over time.

Soils can be naturally acid or alkaline, and this can be measured by testing their pH value.

Having the correct pH is important for healthy plant growth. Being aware of the long-term effects of different soil management practices on soil pH is also important. Research has demonstrated that some agricultural practices significantly alter soil pH.

The development of strongly acidic soils (less than 5.5 pH) can result in poor plant growth as a result of one or more of the following factors:

- Aluminium toxicity.
- Manganese toxicity.
- Calcium deficiency.
- Magnesium deficiency.
- low levels of essential plant nutrients such as phosphorus and molybdenum.

Alkaline soils may have problems with deficiencies of nutrients such as zinc, copper, boron and manganese. Soils with an extremely alkaline pH (greater than 9) are likely to have high levels of sodium.

The correct balance is where the soil pH is between 5.5 and 7.5, so every effort should be taken to check soil pH levels regularly. Early identification of soil pH problems is important as it can be both costly and difficult to correct long-term nutrient deficiencies.

Changing soil pH

Some fertilizer can change soil pH and increase or reduce the amount of nutrients available to plants.

Fertilizer such as crushed sulfur and some ammonium-based nitrogen Fertilizer lower pH and make soil more acid. They are, therefore, useful for soils with problems caused by high pH.

Lime and dolomite

When soils are too acidic for a particular crop, lime or dolomite can be used to increase the pH to the desired level. The amount of lime or dolomite required to correct an acidic pH will vary from soil to soil.

Soils with high organic matter and clay content will be more resistant to changes in pH and will require larger application rates. Therefore, soil pH, while indicating the need for lime, is not a reliable guide as to how much lime is required.

Trials

Field trials, in which good quality lime was cultivated into the soil surface to a depth of 0.1m, have been undertaken on a number of acidic soils in Queensland.

Across all soils, for every tonne of lime added per hectare, soil pH increased from 0.1 to 0.8 pH units.

The most common change was an increase of 0.2 to 0.3 pH units. The larger pH increases were obtained on sandy soils with low organic matter content.

Commercial applications

Typical commercial application rates of around 2 tonnes of lime per hectare are therefore likely to increase the pH by only about 0.5 of a pH unit.

However, these small pH increases are often enough to result in an increased yield.

Liming tropical and subtropical acidic soils usually results in an increase in their capacity to hold nutrients. This is a benefit that is not often realized.

The most accurate method of determining soil pH is by a pH meter.

Factors affecting soil pH

The pH of a natural soil depends on the mineral composition of the parent material of the soil, and the weathering reactions undergone by that parent material. In warm, humid environments, soil acidification occurs over time as the products of weathering are leached by water moving laterally or downwards through the soil. In dry climates, however, soil weathering and leaching are less intense and soil pH is often neutral or alkaline.

Sources of acidity

Many processes contribute to soil acidification. These are as follows.

- **Rainfall:** Average Rainfall has a pH of 5.6 and is presented as slightly more acidic due to the atmospheric carbon dioxide (that is when combined with water forms carbonic acid which is acidic. When this water flows through soil it results in the leaching of basic cations from the soil as bicarbonates; this increases the percentage of Al^{3+} and H^+ relative to other cations.
- Root respiration and decomposition of organic matter by microorganisms' releases CO_2 which increases the carbonic acid concentration and subsequent leaching.
- **Plant growth:** Plants take up nutrients in the form of ions (e.g. NO^-_3, NH^+_4, Ca^{2+}, $H_2PO^-_4$) and they often take up more cations than anions However, plants must maintain a neutral charge in their roots. In order to compensate for the extra positive charge, they will release H^+ ions from the root. Some plants also exude organic acids into the soil to acidify the zone around their roots to help solubilize metal nutrients that are insoluble at neutral pH, such as iron (Fe).

- **Fertilizer use:** Ammonium (NH^+_4) fertilizers react in the soil by the process of nitrification to form nitrate (NO^-_3) and in the process release H^+ ions.
- **Acid rain:** The burning of fossil fuels releases oxides of sulfur and nitrogen into the atmosphere. These react with water in the atmosphere to form sulfuric and nitric acid in rain.
- **Oxidative weathering:** Oxidation of some primary minerals, especially sulfides and those containing Fe^{2+}, generate acidity. This process is often accelerated by human activity:
  - Mine Soil Severely acidic conditions can form in soils near some mine spoils due to the oxidation of pyrite.
  - Acid sulphate soil formed naturally in waterlogged coastal and estuarine environments can become highly acidic when drained or excavated.

Sources of alkalinity

Total soil alkalinity increases with

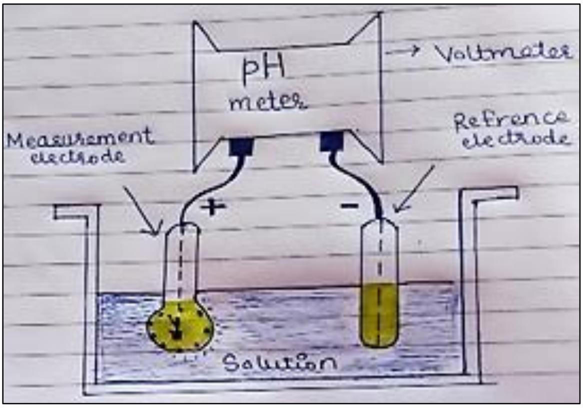
- Weathering of silicate, aluminosilicate and carbonate minerals containing $Na^+Ca^{2+}Mg^2$ and K^+.
- Addition of silicate, aluminosilicate and carbonate minerals to soils; this may happen by deposition of material eroded elsewhere by wind or water, or by mixing of the soil with less weathered material (such as the addition of limestone to acid soils).
- Addition of water containing dissolved bicarbonates (as occurs when irrigating with high-bicarbonate waters).

The accumulation of alkalinity in a soil (as carbonates and bicarbonates of Na, K, Ca and Mg) occurs when there is insufficient water flowing through the soils to leach soluble salts. This may be due to arid conditions, or poor internal soil drainage; in these situations, most of the water that enters the soil is transpired (taken up by plants) or evaporates, rather than flowing through the soil.

The soil pH usually increases when the total alkalinity increases, but the balance of the added cations also has a marked effect on the soil pH. For example, increasing the amount of sodium in an alkaline soil tends to induce dissolution of calcium carbonate, which increases the pH. Calcareous soils may vary in pH from 7.0 to 9.5, depending on the degree to which Ca^{2+} or Na^+dominate the soluble cations.

Principle of PH meter

A pH meter is a scientific instrument that measures the hydrogen-ion activity in solutions, indicating its acidity or basicity (alkalinity) expressed as pH value. The principle of pH meter is the concentration of hydrogen ions in the solution e.g., it is the negative logarithm of a hydrogen ion. Electric device used to measure hydrogen ion activity (acidity or alkalinity) in solution. Fundamentally, a PH meter consists of a voltmeter attached to a pH-responsive electrode and a reference (unvarying) electrode. The pH-responsive electrode is usually glass, and the reference is usually a Silver – silver chloride electrode, although a mercury- mercurous chloride (calomel) electrode is sometimes used. When the two electrodes are immersed in a solution, they act as a battery. The glass electrode develops an electric potential (charge) that is directly related to the hydrogen-ion activity in the solution (59.2 millivolts per pH unit at 25 °C [77 °F]), and the voltmeter measures the potential difference between the glass and reference electrodes.



PH meter

How to use PH meter

Shake off any excess fluid on the device before you place it in the sample liquid or water. Place the device in the sample and press the measure pH button. You should get a stable reading in about two minutes. Get another reading for accuracy.

Equipment for soil pH

pH meter. It consists of two electrodes

a) Glass electrode.

b) B. Calomel electrode (Reference electro).

A. Glass electrode

1) The glass electrode consists of thin-walled bulb of pH sensitive glass, sealed to a stem of high resistance glass. It is better to choose a lower resistance electrode (pH range 0 to 12) with more rapid response and to tolerate the possibility of small errors caused by the reaction between the electrode surface and the film of soil suspension in contact with it.
2) New electrodes should be checked in at least three standard buffers, say near pH 4,7 and 9 linearity of response.
3) The useful life of glass electrode is extended if it is kept moist when not in use. Combined glass and reference electrode should also be stored in a buffer solution, but separate reference electrodes should have their liquid junctions immersed in nearly saturated KCl solution protected from evaporation.
4) With continued use, the performance of glass electrode gradually worsens. Electrode with poor performance should be replaced.
5) Erratic off scale readings indicate very high electrical impedance in the electrical circuit.
6) Air bubbles interrupt the path between the glass bulb and the internal reference electrode. These bubbles are usually dislodged by gentle tapping and shaking.

B. Calomel electrode/Reference electrode

1) These electrodes are usually the calomel type with saturated KCl electrolyte. But Ag-AgCl electrodes give satisfactory service and have an advantage in being easily paired or even constructed in a laboratory.
2) Calomel electrodes must not be heated 70-degree C. They should be closely inspected regularly to see that no air gaps have developed.
3) The liquid junction between the reference electrode and the test liquid usually made with KCl solution, which is also the reference electrolyte. The liquid junction potential with soil suspension is not the same with other electrolytes. The KCl solution used should not be saturated at any temperature above the minimum to which the electrolyte will be subjected. For example, solution of 32g KCl in 100mL water is just undersaturated at 15 degree.
4) The KCl solution should flow through the liquid junction at a very low but detectable rate.

5) The liquid junction of reference electrode should just enter the surface of the soil suspension in order to be in a zone of minimum clay concentration. This makes the junction potential as small as possible and closest to that in the standardizing buffer solution. The difference in the junction potential in the buffer and suspension is included in the pH shown by the meter.

Reagents

1) **Standard buffer solution, pH 4.00:** Prepare stock solution of 0.3 M potassium hydrogen phthalate by dissolving 15.3 g of the analytical grade salt in about 225 mL of hot water, cooling the solution, and diluting it 250 mL. Add a drop of toluene to discourage the growth of micro-organisms. For the standard buffer pH 4.0, a mix 100 mL of the stock solution with 500 mL water. Prepare the fresh solution every week.
2) **Standard buffer solution, pH 9.2:** Dissolve 3.81 g sodium tetraborate (AR) in water and dilute to 1000 mL.
3) **1.0 N Potassium chloride solution (AR):** Dissolve 74.56 g of KCl in water and make up the volume to 1000 mL.

Apparatus

Electrometric pH meter with glass and calomel electrodes.

Procedure

1) Soil: water, 1:2.5, soil: KCl, 1:2.5.
2) Weight 20g air-dry soil into beaker and add 50 mL distilled water. Stir at regular intervals for one hour.
3) In the meantime, turn the pH meter on, allow it to warm up, and standardize the glass electrode using both the standard buffers. Remember to adjust the temperature compensation knob to the temperature of the solution. Measure the pH of the sample suspension, stirring the suspension well just before introducing the electrodes.
4) Rinse the electrodes after each determination with water carefully but do not blot them dry with filter paper before the next determination. Standardize the glass electrode after every ten determinations.
5) To determine pH in 1.0 N KCl, use 50 mL of 1.0 N KCL instead of water. Stir at regular intervals for one hour. Let it settle and measure the pH of the clear supernatant solution.

6) pH meter. It consists of two electrodes.

c) Glass electrode.

d) B. Calomel electrode (Reference electrode).

C. Glass electrode

1) The glass electrode consists of thin-walled bulb of pH sensitive glass, sealed to a stem of high resistance glass. It is better to choose a lower resistance electrode (pH range 0 to 12) with more rapid response and to tolerate the possibility of small errors caused by the reaction between the electrode surface and the film of soil suspension in contact with it.
2) New electrodes should be checked in at least three standard buffers, say near pH 4,7 and 9 linearity of response.
3) The useful life of glass electrode is extended if it is kept moist when not in use. Combined glass and reference electrode should also be stored in a buffer solution, but separate reference electrodes should have their liquid junctions immersed in nearly saturated KCl solution protected from evaporation.
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D. Calomel electrode/Reference electrode

1) These electrodes are usually the calomel type with saturated KCl electrolyte. But Ag-AgCl electrodes give satisfactory service and have an advantage in being easily paired or even constructed in a laboratory.
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Reagents

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3) **1.0 N Potassium chloride solution (AR):** Dissolve 74.56 g of KCl in water and make up the volume to 1000 mL.

Apparatus

Electrometric pH meter with glass and calomel electrodes.

How to calibrate a pH meter

1) Examine the pH electrode. First, check the pH electrode for contamination or damage.
2) Flush the pH sensor. Next, flush your sensor with distilled water.
3) Immerse the pH electrode.
4) Calibrate the pH meter.
5) Rinse the pH sensor and repeat.

Procedure

1) Soil: water, 1:2.5, soil: KCl, 1:2.5.
2) Weight 20g air-dry soil into beaker and add 50 mL distilled water. Stir at regular intervals for one hour.

3) In the meantime, turn the pH meter on, allow it to warm up, and standardize the glass electrode using both the standard buffers. Remember to adjust the temperature compensation knob to the temperature of the solution. Measure the pH of the sample suspension, stirring the suspension well just before introducing the electrodes.
4) Rinse the electrodes after each determination with water carefully but do not blot them dry with filter paper before the next determination. Standardize the glass electrode after every ten determinations.
5) To determine pH in 1.0 N KCl, use 50 mL of 1.0 N KCL instead of water. Stir at regular intervals for one hour. Let it settle and measure the pH of the clear supernatant solution.

Result

In this way we can measure the PH of the soil by using PH meter.

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Chapter - 3

Recent Developments in the Synthesis of 4-Hydroxyphenyl Glycine and its Derivatives

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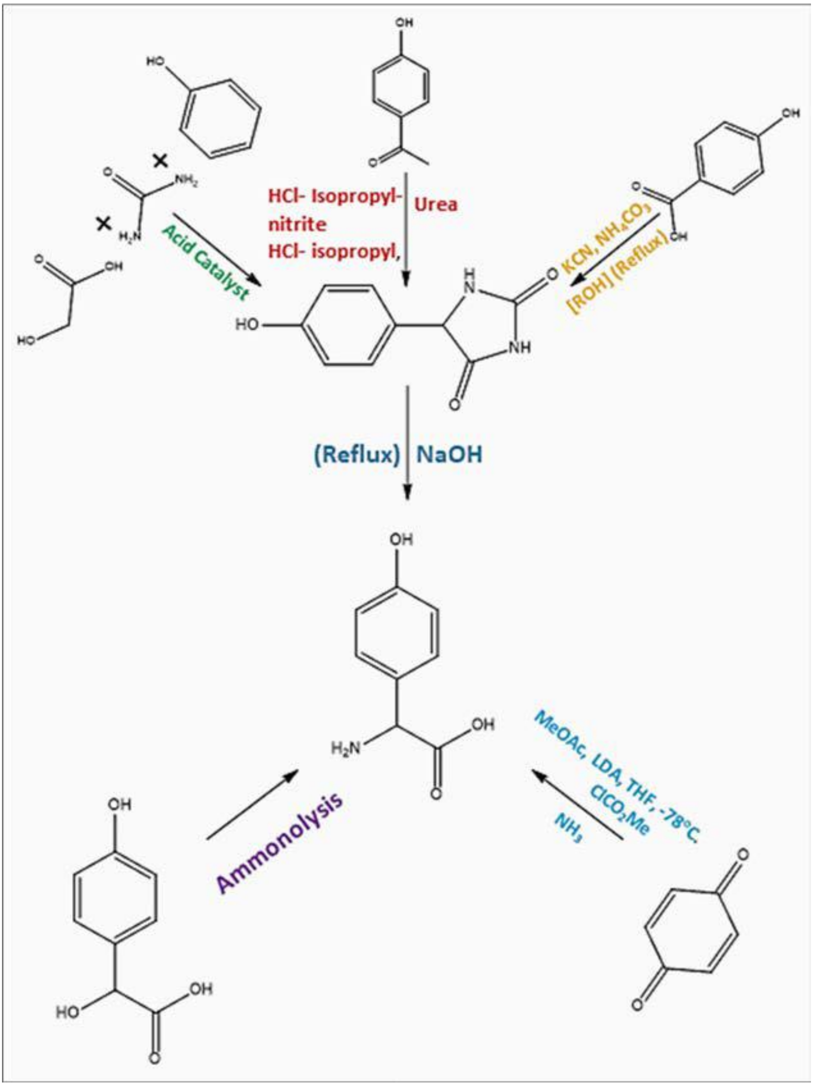
Chapter - 3

Recent Developments in the Synthesis of 4-Hydroxyphenyl Glycine and its Derivatives

Rutvi Mistry and Mahesh Vasava

Abstract

p-Hydroxyphenyl glycine (p-HPG) is an important intermediate in synthesis of vancomycin class of antibiotics. It is a non-proteogenic amino acid. Several pathways are available to synthesize p-HPG. There are mainly three pathways, one through 5-(4'-Hydroxyphenyl) hydatoin intermediate, the second one via p-hydroxymadalic acid intermediate, and the third pathway involves p-benzoquinone as a chief reactant. The 5-(4'-Hydroxyphenyl) hydatoin intermediate can be synthesize three ways. In this work, we highlight recent developments in the synthesis of p-Hydroxyphenyl glycine (p-HPG). We also describe the pathways and an overview on derivatives of p-HPG.

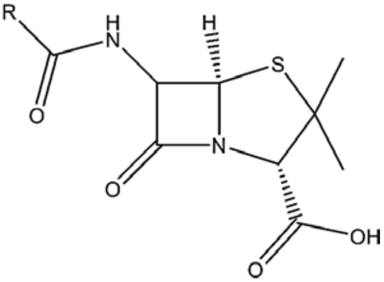


Outline overview of synthesis of p-HPG

Keywords: p-Hydroxyphenylglycine, p-Hydroxyphenylglycine Ester, Esterification, 5-(4’-Hydroxypheny -l) hydatoinby, p-Hydroxymadalic acid, p-Benzoquinone, Amoxicillin.

Introduction

The Discovery of penicillin is one of the greatest achievements of the science field. It changes the medicinal world and infectious disease research. Also gave a new direction to microbiology, medicinal chemistry, and molecular biology [1-17]. Late 19th century was suffering from bacterial and fungal infection [18]. In 1928 Alexander Fleming isolated the penicillin which comes from the Penicillium genus. In 1929 he published a paper on his discovery. There was no work done around almost a decade for isolation of the *Penicillium* genus. In 1939 Howard Florey and team successfully grew the *Penicillium* genus and also isolated them. 25 May 1939 an experiment was performed on mice by giving penicillin injections which was a successful experiment where all treated mice were alive [19]. Penicillin is considered as a bactericidal meaning that it kills the bacteria. It was not only bactericidal but also it destroyed the concentration of certain leukocytes constitutes which are defence agents of bacteria [20-26].



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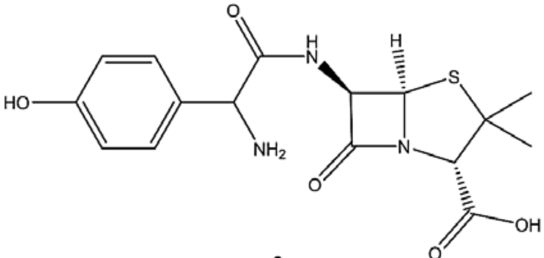
Scheme 1. Structure of penicillin

Penicillin *In vivo* study did on mice where scientist note some side effect of penicillin. Also found that degree of degradation of penicillin was slow and with some limitations. On human trial the scientists also found that 10 to 40% patients not get cured also not by giving larger doses for many weeks. In the end scientist conclude that penicillin is not able completely deactivate the bacterial colony [27-32]. A research the reason of not completely capable of deactivating bacteria was that some of the bacteria had grown b-lactamases enzyme. This enzyme destroys beta-lactams before they can inactivate the bacterial cell wall [33].

Penicillin was not completely able to deactivate bacteria so furthermore research had been done on penicillin. The research was on fond a β-lactamase inhibitor by this penicillin regain the antibacterial activity. Penicillin is fusion of 4-membered β-lactam ring and 5-memberd thiozolidine ring and an acyl group attach to β-lactam ring which is essential for biological activity [33]. The possibility of the R group chooses the drug's robustness to enzymatic what's more, acidic hydrolysis and its activity against different microorganisms. Adjustment of the R group, for example, the expansion of bulky side chains or effective gatherings gives various variations of penicillins that are known to improve movement, show obstruction to penicillinase, and are more impervious to corrosive [34]. Altering the R groups by expanding the side chain or putting a bulky group gives numerous modification of penicillin which will be more effective also cover the wide range of bacteria. For example Benzylpenicillin, oxacillin, azlocillin, mezlocillin, amoxicillin, ampicillin, penicillin G etc.

In 1972 scientist of Beecham Research Laboratories discovered Amoxicillin from Ampicillin. It is a semi-synthetic aminopenicillin drug. This drug is having a broad-spectrum range of gram-positive and gram-negative bacteria to deactivate. Amoxicillin has a good absorption capacity. Amoxicillin has been largely used in veterinary medicine [34].



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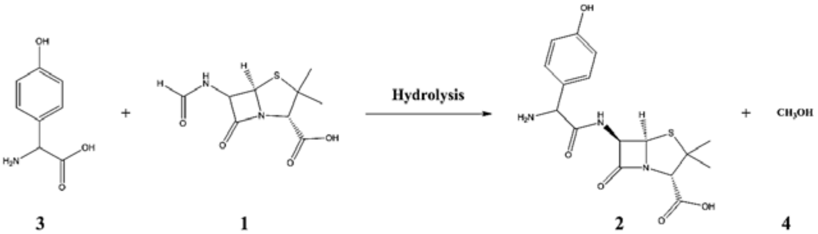
Scheme 2. Structure of Amoxicillin

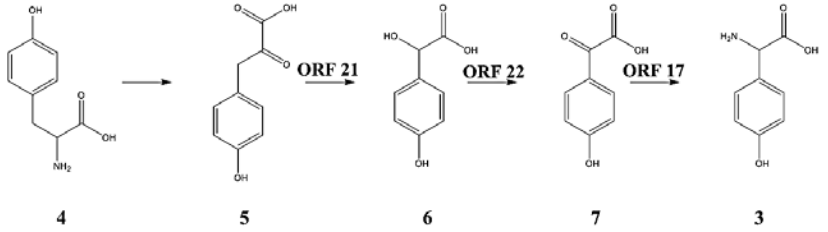
Amoxicillin is a derivative of penicillin where the penicillin gets substituted at 6th position of the penam ring by p-Hyroxyphenylglycine (p-HPG). Amoxicillin is synthesis from penicillin and p-HPG by the hydrolysis.



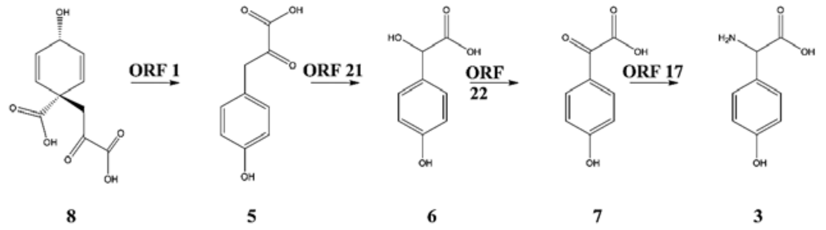
Scheme 3. Outline of synthetic pathway of Amoxicillin

Also, p-HPG is used as core structure in vancomycin, chloroeremomycin, complestatin etc., which plays primary part in structural part. Here p-HPGE is conjugate acid in amoxicillin. The mechanism of action of amoxicillin is that this beta-lactam ring interferes in the biosynthesis of peptidoglycan which is one of the constituents of the bacterial cell wall. Peptidoglycan is maintaining the integrity, also some vital processes. This peptidoglycan contains two alternative amino sugar, N-acetyl glucosamine and N- acetylmuramic acid, and 5 peptides of amino acids ending in D-Alanyl-DAlanine and attached to the N-acetylmuramic acid. Rigid stability provides by this polymer due to its highly cross-linked structure. In bacterial cell wall protein penicillin binding protein –A1 (PBP-1A) is getting bind to amoxicillin binding penicillin. By acylation of C terminal domain of trans peptidase which is getting inactive due to penicillin-sensitive. Amoxicillin structure is similar to D-Alanyl-D-Alanine. So easily gets interact. This inhibition occurs in the last step of synthesis of the bacterial cell wall, preventing the cross-linking of peptidoglycan chains and making structure destabilize. From the upper mechanism, the p-hydroxyphenyl glycine is used by microorganisms. Which helps to synthesize cells of bacteria and when p-HPG attach with penicillin which forms amoxicillin. So, the structure of p-HPG taken by bacteria and penicillin block the formation of the cell wall of bacteria [35-36].

From the upper mechanism, the p-hydroxyphenyl glycine is used by microorganisms. Which helps to synthesize cell of bacteria and when p-HPG attach with penicillin which forms amoxicillin. So, the structure of p-HPG taken by bacteria and penicillin block the formation of the cell wall of bacteria [37]. In 2000, Hubbard at al conclude that p-HPG in microorganism synthesize from tyrosine and prephenate [38].



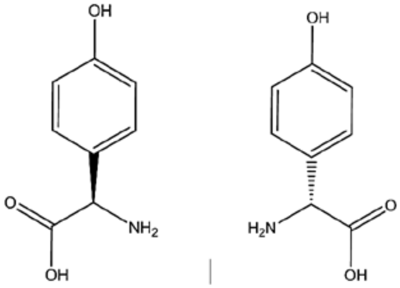
Scheme 4. Outline of biosynthetic pathway for the nonproteinogenic amino acid L-p-hydroxyphenylglycin from tyrosine [38].



Scheme 5. Outline of biosynthetic pathway for the nonproteinogenic amino acid L-p-hydroxyphenylglycin from prephenate [38].

p-HPG is p-HPG is a non-proteinogenic amino acid. Non-proteinogenic amino acids are non-natural encoded and also not found in genetic code of any organism. This non-proteinogenic activities arise from natural proteinogenic amino acid which gets incorporated into the growing peptide chain by the non-ribosomal peptide synthetases (NRPSs) which are followed by downstream modification of residue by this reaction epimerization, terminal methylation, oxidation, cyclization etc [39-44].

p-HPG IUPAC name is 2-amino-2-(4-hydroxyphenyl) acetic acid. Molecular formula is $C_8H_9NO_3$. Molecular weight of p-HPG is 167.16g/mol. p-HPG is optically active. D and L both conformers are available. D-p-HPG is the D-enantiomer. L-enantiomer is found in Herpetosiphon aurantiacus as a non-prteinogenic amino acid.

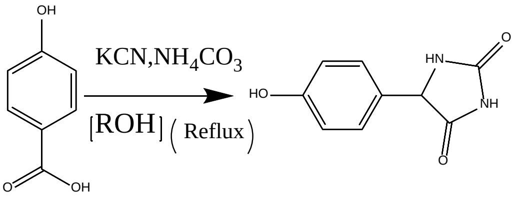


Scheme 6. D-L Conformers of p-Hydroxyphenyl Glysine

Synthesis Revolution of p-HPG and its derivatives

There are many different pathways to the synthesis of p-HPG. Using different reagents and different conditions p-HPG and its derivatives can be synthesized.

In 1944 by Harvil and Herbst discovered the first synthesis of p-Hydroxyphenyl glycine by using the Bucherer- berg reaction. In this pathway they are using CN salt, ammonium bicarbonate, p-hydroxybenzaldehyde. This reaction forms hydroxyphenyl hydantoin which becomes an important intermediate to synthesis p-hydroxyphenyl glycine. To form p-hydroxyphenyl glycine hydrolysis has been done on the intermediate product, the mixture is refluxed with NaOH and then after by acid catalysed esterification with in methanol solvent to form p-Hydroxyphenylglycine ester [45].



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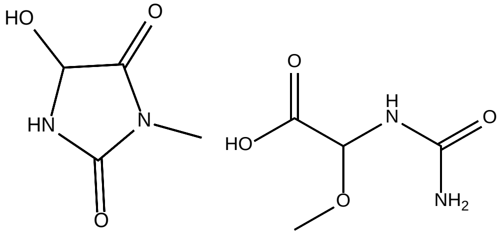
Scheme 7. Outline of synthesis of 5-(4’-Hydroxyphenyl) hydatoin by Harvi and Herbst

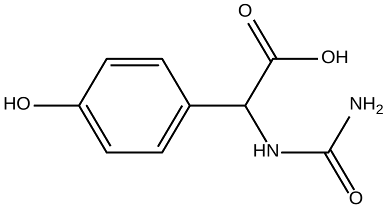
The disadvantages of reaction were the starting materials i.e., p-Hydroxybenzaldehyde which was costly and KCN which is highly toxic. To avoid these disadvantages, Beecham group came up with new synthesis pathway.

This European patent describes process of preparation of hydroxyphenyl hydantoin and hydroxyl phenyl glycine and its derivatives. Here synthesis of hydroxyphenyl hydantoin and hydroxyphenyl glycine are synthesized from glyoxylic acid, urea and phenol in presence of acid catalyst in aqueous medium. Also, in past, these reagents used in different combination of reagent and solvent to synthesize p-Hydroxyphenyl hydantoin. For example: Ben-Ishai *et al* reacted substituted urea ($NH_2CONHCH_3$) with glyoxylic acid to give the formula 1.



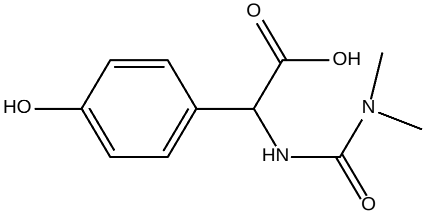
(Formula 1- 2)

Then glyoxylic acid reacts with urea in alcoholic medium giving non-cyclic compound with formula 2 [46]. Then, in British patent, by Smithkline group, prepared n-carbamyl-2-(p-hydroxyphenyl) glycine by using phenol, glyoxylic acid and urea without solvents. And gives the formula 3 [47].



(Formula 3)

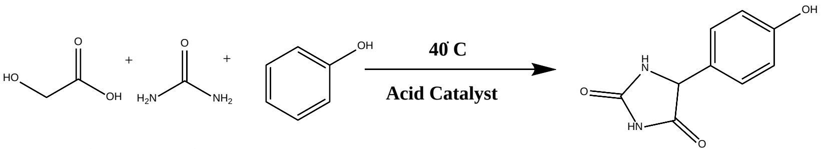
Also Ben at al described the preparation of N-carbamyl-p-hydroxyphenyl glycine (Formula 4) by reaction of phenol with substituted urea-glyoxylic acid adduct [46].



N-carbamyl-p-hydroxyphenyl glycine

Scheme 8. Formula are frailer to synthesis4- hydroxyl phenyl hydantoin

In European patent, they used suitable catalysts like H_2SO_4, HCl, HBr. And as solvent, they used water with miscible polar organic solvents like acetic acid. The rate of reaction was dependent on the quantity of catalyst use and the temperature of reaction. The reaction take around 20 hours to get completed. The reaction proceed into two steps, first glyoxylic acid and urea reacts and then after phenol added into reaction. The quantity of phenol was used excess. Comparing the mole ratio of phenol and glyoxylic acid was 2:1 and the phenol and urea was 2:1 to 1.5. Hydantoin gets precipitated during reaction which is taken out by filtration. After filtration, to remove excess of phenol, the precipitate were washed with distilled water. To convert into p-HPG, pyrolysis/hydrolysis of 5-(4'-Hydroxyphenyl) hydatoinwas done. The hydrolysis can be done in alkaline or acidic medium. Mostly alkaline hydrolysis was preferable. For alkaline medium as base, sodium hydroxide and potassium hydroxide were used. Water was used as solvent. Temperature must be about at reflux temperature and isolation was carried by neutralizing the pH and precipitates were formed.



12 13 14 10

Scheme 9. Outline Synthesis of 5-(4’-Hydroxyphenyl) hydatoinby Beecham group

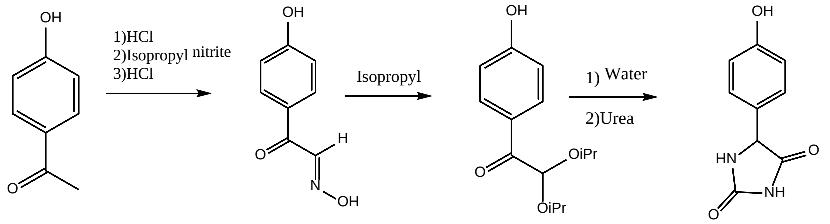
Here in this reaction author used different acid catalyst which were HCl, HBr, H_2SO_4. All this catalyst gives different amount of product.

Table 1: Comparison of Acid Catalyst and amount of product

Catalyst	Amount of Product
Sulphuric acid	22.9%
Hydrobromic acid	28.14%
Hydrochloric acid	48%

From the table most suitable catalyst is Hydrochloric acid comparing with the other acids. The maximum amount of product was obtain 48% by Beecham group [47-48].

US patent No. 07/451,675 filed a patent on production of 5-(4’-Hydroxyphenyl) hydatoin and D-p-Hydroxyphenylglycine from 4-Hydroxyacetophenone. So, in previous two patent CN salt use according to Bucherer – Berg’s reaction. And in European patent pathway uses glyoxylic acid, urea and phenol in presence of acid catalyst to synthesize 5-(4’-hydroxyphenyl) hydantoin but reaction required moderating to high temperature range and also the theoretical yield amount is very low. Also, for the esterification, product must be optically active. In this synthesis the material or chemical used are C_2 to C_5 alkyl nitrite component which is preferably isopropyl nitrite or t- butyl nitrile amount of 4-hdroxyacetone. The composition of alcohol must be C_4 or less of secondary alcohol which is present in excess of amount. Hydrochloric acid present 1 to 2 moles equivalent to isopropyl. Water and urea add to to reaction to form hydatoin. [49].



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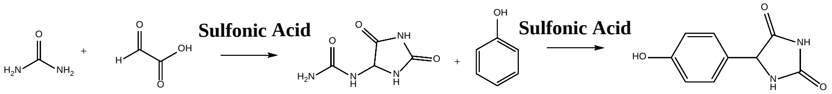
Scheme 10. Outline Synthesis of 5-(4’-Hydroxyphenyl) hydatoinby US patent [49].

Following this synthetic pathway the amount of product was maximum 74% [49].

Carlos Cativiela *at at* use different Catalyst to sytnesize 5-(4’-Hydroxyphenyl) hydatoin. Previous all the reaction have one drawback which was they does not provide good selectivity of O/P position. Here author used sulfonic acid resine Dowex in place of mineral acids. Sulfonic Acid increases the selectivity towards para position.

Here there are two routes were available to synthesize 5-(4-hydroxyphenyl) hydantoin. In Scheme11 route no 1, first urea and glyoxylic acid were reacts by forming allantoin which further reacts with phenol. But here in this step ortho/para selectivity was so low comparing to direct one-step synthesis [50-53].

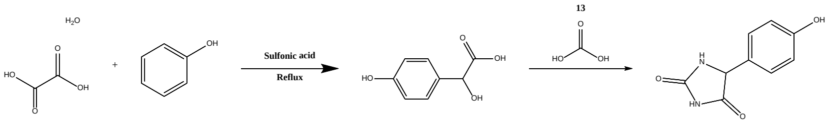


13 **12** **19** **14** **10**

Scheme 11. Outline Synthesis of 5-(4’-Hydroxyphenyl) hydatoinby Carlos Cativiela *at al*

(Route no.1)

In scheme 12 route no 2, phenol reacts with glyoxalic acid forms p-Hydroxtmadalic acid which further reacts with urea and forms 5-(4’-Hydroxyphenyl) hydatoin. So here the issue of selectivity is shifted to the reaction of phenol and glyoxylic acid to produce hydroxymandelic acids. The para product possible only in basic condition which was note in synthesis of p-hydroxymadelic acid. The yield was obtain 96% [54-64].

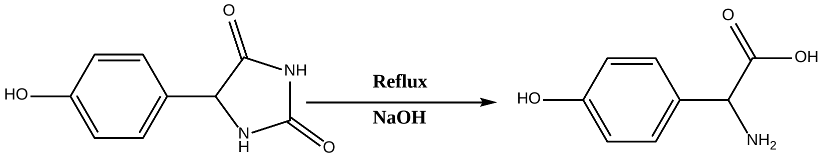


12 **14** **18** **10**

Scheme 12. Outline Synthesis of 5-(4’-Hydroxyphenyl) hydatoinby Carlos Cativiela *at al*

(Route no.2)

To synthesize p-Hydroxyphenyl glycine, Hydrolysis of 5-(4’-Hydroxyphenyl) hydatoin has been done. In hydrolysis procedure 5-(4’-Hydroxyphenyl) hydatoin on reflux with solution of NaOH. 92% yield was obtain [49].

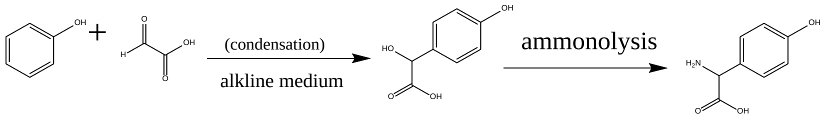


10 **3**

Scheme 13. Outline Synthesis of p-hydroxyphenyl glycine

Netaji P. Powar found out a new pathway to synthesize p-hydroxyphenylglycine. In this synthesis the intermediate 5-(4’-Hydroxyphenyl) hydatoin replace by p-hydroxymandelic acid. Strecker's amino acid method' or the hydantoin route are two traditional techniques for preparing intermediate. From an industrial standpoint, one of the methods based on the condensation of phenol with glyoxylic acid looks to be highly promising.

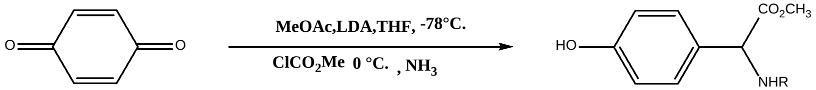
Synthesis of p-HPG by using ammonolysis of p-hydroxymadalic acid, to obtained p-hydroxymadalic, condensation of phenol and glyoxalic acid. After that ammonolysis of p-hydroxymadalic acid. In this synthesis Phenol and glyoxylic acid reflux under alkaline condition. To synthesize p-hydroxyphenyl glycine. For ammonolysis ammonia aqueous solution used. By this reaction they are the theoretical obtain was 91% as p-hydroxymadalic acid and p-hydroxyphenyl glycine obtaine 83% [65-71].



14 **12** **18** **3**

Scheme 14. Outline Synthesis of p-hydroxyphenyl glycine by Netaji P. Powar

Author Gerardus *at al* synthesize new route of p-HPG preparation. The preparation of p-HPG by Strecker synthesis involves hydantoin route also by amminolysis of p-hydroxymandelic of phenol and glyoxylic acid, p-hydroxymandelic acid gives p-HPG. But in this routes product forms in para and ortho product due to OH group is ortho-para directing. To prevent ortho as starting material p-hydroxy benzaldehyde use which is so expensive. To resolve this problem here author changes the route of reaction by using p-benzoquinone. In this synthesis para position is already highly reactive due to carbonyl carbon. In step-1 p-Benzoquinone is mixed with methyl lithioacetate in presence of lithium diisopropylamide, Tetrahydrofuran and methyl chloroformate and kept on stirring at very low (in minus) temperature. The precipitation increases till temperature. Intermediate will be formed i.e. methyl 2-(1-((methxycarboyl)oxy)-4 oxocyclo-hexa-2,5 dine-1-yl)acetate. And at low temperature and then add THF then put Condenser add Methyl acetate before add dissolve it in THF [72].



20 **21**

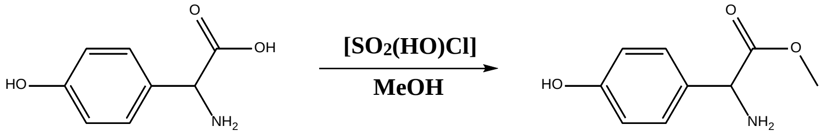
Scheme 15. Outline Synthesis of p-hydroxyphenyl glycine by Gerardus *at al*

This synthesis of p-HPG by using low cost reactant p-benzoquinone. Also on resolving the ortho-para product problem and only gives para product.

Table 2: Theoretical yield of p-HPG and its derivatives [72]

Derivatives product no. 18	R Group	Product amount
A	H	80-90%
B	CH_2Ph	95%
C	$(CH_2)_3CH_3$	100%
D	$C_6 H_{11}$	99%
E	$C(CH_3)_3$	92%
F	Piperidine	87%

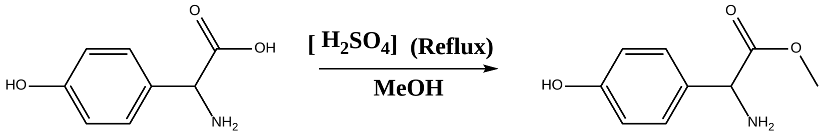
Furthermore, Peter Jan Leonard M Quaedflieg, Wilhelmus Hubertus Jos Boesten filed a patent on Esterification amino acids and peptides where they describe the esterification of p-HPG. Initially the esterification was done by using hydrosulfate, drawback of this reaction was that the amount of hydrosulfate required 2 equivalent of reactant which gave 93-94% of yield and also required long period of time. So, in this patent Esterification done by using Chlorosulfonic acid and methanol. Completion time was one hour of (DL)-p-HPG [73-77].



3 **22**

Scheme 16. Outline of esterification of p-HPG by Peter Jan Leonard M Quaedflieg, Wilhelmus Hubertus Jos Boesten

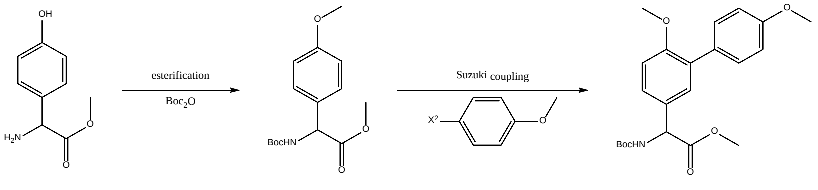
CI San Sebastian filed patent on process for the synthesis of Hydroxyphenylglycine Ester. Author synthesis the crystal form of D-p-HPG Ester. The drawback of Peter Jan Leonard M *at al* patent was that the product was obtain racemic. In this patent they used sulphuric acid and methanol and reaction was put on reflux for two hours and neutralize with NaOH solution. The isolated yield of the products was 95% [78].



3 **22**

Scheme 17. Outline of esterification of p-HPG by *CI* San Sebastian

From p-HPG Ester, using Suzuki coupling reaction binary derivative can be synthesize. The product is naturally found I chloropeptin family. Monica Prieto, Silvia Mayor, Paul Lloyd-Williams, and Ernest Giralt found the route by Suzuki coupling [79].

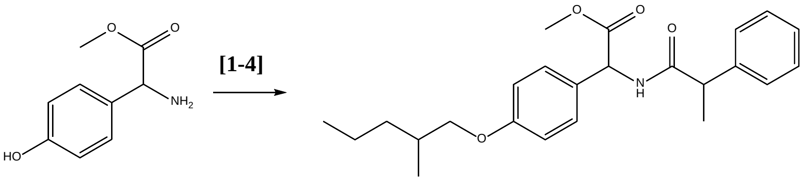


22 **23** **24**

Scheme 18. Outline of binary derivative of p-HPG Ester synthesize by Suzuki Coupling

(X^2 = Br or Bpin) [79].

p-HPG derivative [(2s)-N-(1R)-2-amino-1-4-(2-methlpentyloxyphenyl) ethyl-2-phenylpropan –amide] use as GPR88 agonist. It is synthesis from p-HPG Ester. The reaction needs four steps to get complete which has been show in scheme 19. The isolated yield of the products was 45% which is very low [80].

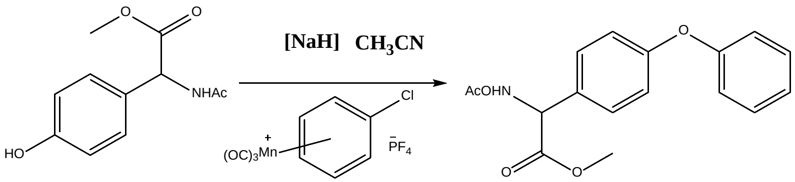


22 25

Scheme 19. Outline synthesis of [(2s)-N-(1R)-2-amino-1-4-(2-methlpentyloxyphenyl)ethyl-2- phenylpropan –amide] [80].

Where [1] = Boc$_2$, DCM, DIPEA, [2] = PPh$_3$, THF,CBr$_4$, DEAD, 2-methylpentanol, [3] = DCM, TFA, [4] = HBTU, TEA, MeCN, (*S*)-2-phenylpropionic acid

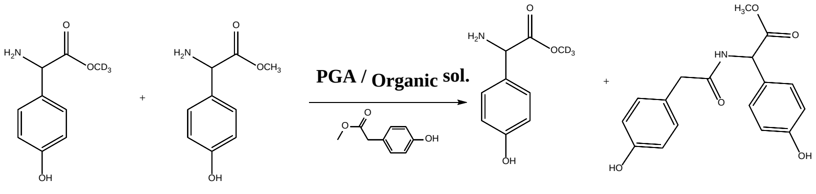
Diaryl and polyaryl ethers are essential components in a wide range of natural products, the most frequent technique for forming the ether bond, namely Ullman coupling, only works under extremely severe circumstances. Methyl 2-(acetoxyamino)-2-(4-phenoxyphenyl)acetate is a natural Olefin product. Anthony J. Pearson, Paul R. Bruhn, and Shih-Ying Hsu synthesize pathway from N-Acetyl-4-(phenyloxy)phenylglycine Methyl Ester which is derivative of p-HPG Ether [81].



26 27

Scheme 20. outline synthesis of Diaryl Ethers [81]

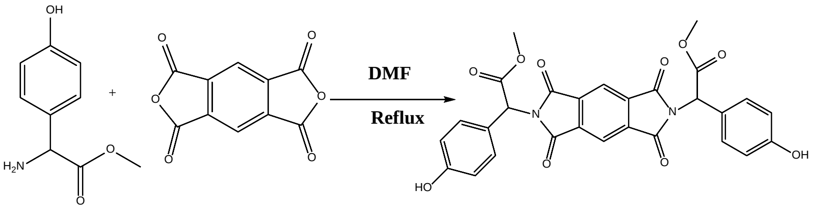
Penicillin G intermediate methyl 2-(4-hydroxyphenyl)-2-(2-(4-hydroxyphenyl)acetamido) acetate is derivative of p-HPG Ether Alessandra Basso, Paolo Braiuca, Luigi De Martin, Cynthia Ebert, Lucia Gardossi and Paolo Linda found a pathway to synthesize b hydrolytic reaction of p-HPG ester [82].



27 22 28 29

Scheme 21. Outline synthesis of methyl 2-(4-hydroxyphenyl)-2-(2-(4-hydroxyphenyl)acetamido) acetate [82].

Bisphenol-A or 2,2-bis(4-hydroxydiphenyl)propane use in to increase mechanical strength and stiffness of polymer. It is because their aromatic backbone architectures may considerably enhance the stiffness and mechanical strength of produced polymers, they are high-performance materials. N,N′-(pyromellitoyl)-bis-D-4-hydroxyphenylglycinedimethyl ester monomer of Bisphenol-A and also derivative of p-HPG Ester. Farhang Tirgira, Mohammad R. Sabzalian and Ghasem Moghadam synthesize,2-bis(4-hydroxydiphe nyl)propane from p-HPG Ester and Pyromellitic dianhydride [83].



22 30 31

Scheme 22. Outline Synthesis of N,N-(pyromellitoyl)-bis-D-4-hydroxyphenylglycinedimethyl ester [83].

Conclusion

Harvil and Herbst used Bucherer-Berg reaction mechanism to synthesize 5-(4’-Hydroxyphenyl) hydatoin intermediate by using cyanide salt which is toxic in nature. To overcome the side effect, Beecham group came up with new synthesis pathway of 5-(4’-Hydroxyphenyl) hydatoin, which uses urea, glyoxylic acid, phenol but this reaction does not give good amount of Yield. So, an US patent changed the intermediate to 4-hydroxyacetophenone. However, this reaction failesto provide sufficient yield and therefore, Netaji P. Powar & Sampatraj B. Chandalia discovered synthesis of p-HPG by using the ammonolysis of p-hydroxymadalic acid which is obtained by condensation of phenol and glyoxalic acid and of yield sufficiently high. But reaction dose not gives selectivity between ortho and para position. Hence author Gerardus *at al* synthesize new route by using p-Benzoquinone, which is also cost effective material, but this synthesis need extremely aggressive conditions. To overcome the drawback Carlos C. *at al* replace the mineral acid catalyst to sulfonic acid in Beecham group method, its increases the selectivity towards para position.

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Chapter - 4

Green Approach for Biosynthesis of Copper and Copper Oxide Based Nanomaterials Using Plant Extracts and their Application in Antimicrobial Activity

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Chapter - 4

Green Approach for Biosynthesis of Copper and Copper Oxide Based Nanomaterials Using Plant Extracts and their Application in Antimicrobial Activity

D.T. Sakhare

Abstract

Recent development in nanoscience and nanotechnology has contributed to the wide applications of metal and metal oxides nanoparticles in several field of sciences, research institutes and industries. Among all metal oxides, copper & copper oxide nanoparticles has gained more attention due to its distinctive properties and applications. The high cost of reagents, equipment and environmental hazards associated with the physical and chemical methods of synthesizing opper & copper oxide nanoparticles has been a major setback. In order to puffer solution to the aforementioned challenges by reducing environmental pollution and production of cheaper nanoparticles with good properties and efficiency, this review focus on collection of comprehensive information from recent developments in the synthesis, characterization and applications from previous scientific findings on biological method of synthesizing opper & copper oxide nanoparticles due to the acclaimed advantages of been cheap, environmentally friendly, convenient and possibility of been scale up in into large scale production reported by numerous researchers. Our finding also support the synthesis of opper & copper oxide nanoparticles from plant sources due to relative abundance of plants for the production of reducing and stabilizing agents required for opper & copper oxide nanoparticles synthesis, potential efficiency of plant biomolecules in enhancing the toxicity effect of opper & copper oxide nanoparticles against microbes, prevention of environmental pollution due of nontoxic chemicals and degradation effectiveness of opper & copper oxide nanoparticles synthesized from plant sources. Furthermore, this study provide useful information on the rapid synthesis of opper & copper oxide nanoparticles with desired properties from plant extracts.

Keywords: Green synthesis, copper & copper oxide nanoparticles, antimicrobial activity.

1. Introduction

Nanoparticles (NPs) are materials ranging in size from 1–100 nm, with unique properties compared to bulk materials. Their higher surface-area-to-volume ratio is a very important unique property that allows them to be used in different fields of chemical, food, electronic, and healthcare industries. Copper is one of the indispensable micro elements obligatory for the growth and development of plant. It can be present as Cu^{2+} and Cu^{+} under natural conditions. Optimum concentration is regularly involved in the plants, ranging from 10^{-14} to 10^{-16} M. In addition to many of its important functions such as cell wall metabolism and protein regulation, it also acts as secondary signaling molecule in plant cells. It takes part in the mitochondrial respiration, photosynthetic electron transport, iron mobilization, hormone signaling, oxidative stress response, and also acts as co-factor for many enzymes [1]. In recent years, the development of an efficient "green" chemistry method for synthesizing metal NPs has become a major focus of researchers. Green synthesis of Cu and CuONPs is more advantageous than chemical and physical synthesis as it is a clean, nontoxic, cost-effective, and environmentally friendly approach. It bypasses the use of harsh, toxic, and expensive chemicals [2] and, instead, utilizes biological entities like bacteria [3], yeasts [4], fungi [5], algae [6], and plants. Among all these natural organisms used in the green synthesis of Cu and CuO NPs, plants rich in bioactive compounds can serve as a reducing, stabilizing, and capping agent during NP synthesis; this makes them the best choice. They are nonpathogenic to humans, and the downstream processing steps are simple [7]. Unlike some bacterial and fungal strains that produce the NPs intracellularly, plant-mediated NP synthesis yields the NPs in the mixture solution, which can be easily obtained by filtering, rinsing, and drying [8]. The size, morphology, and stability of NPs can also be easily optimized for medicinal and pharmaceutical usage using this green method [9]. In this review, we focus on the updates of Cu and CuO NPs synthesized from plants and their medicinal application.

Metallic nanoparticles are multifunctional in nature and hence finds huge number of applications in various sectors for environmental, biomedical and antimicrobial, solar power generation and catalytic causes. Application of plant extracts to synthesize copper and its oxide nanoparticles is a green chemistry methodology which establishes strong relationship between natural plant material and nano-synthesis. It has been reported in the past study that copper, gold and silver nanoparticles exhibited excellent antimicrobial activity against various disease causing pathogens. In recent years, copper nano particles (Cu NPs) have gained significance due to their multifunctional uses in industries and medicine. However, other nanoparticles, such as platinum, gold, iron oxide, silicon oxides and nickel have not shown bactericidal effects in studies with Escherichia coli [10]. The antibacterial study on E. coli and Bacillus subtilis using Cu and Ag NPs, revealed the fact that Cu exhibited superiority over Ag. Cu NPs have wide applications as heat transfer systems antimicrobial materials, sensors and catalysts. In addition, copper and its compound have been applied as antifungal, antiviral, and molluscicidal agents. The synthesis of Cu NPs by using extracts of various plants found all over the globe have been reported by many researchers in the past [11]. It is essential to develop clean, reliable, biocompatible, cheap, and nontoxic green method of nanoparticle's synthesis. Many plants parts or whole plants have been used for the green synthesis of Cu NPs due to the presence of large number of bioactive compounds in plants. The extracts of plants *Neriumoleander*, *Punica granatum*, *Aegle marmelos* & *Ocimum sanctum*, [12] *Zingiber officinale* have been efficiently applied for this purpose.

Copper oxides by themselves are hazardous, and in order to remove this toxicity and make them suitable for human consumption, they are refined through a series of procedures that include treatment with plant extracts and some animal fluids. Thus, synthesizing nanoparticles from medicinal plants will benefit their application in the biomedical arena. Additionally, the natural antibacterial capabilities of plant extracts increase the qualities of green nano-materials generated utilizing plants. It is vital to develop a diverse array of antimicrobials that are both affordable and readily available. Plants are abundant and can be used to synthesize nano-materials. The flowchart in Figure.1 illustrates the overall procedure for the production and application of Cu/CuO-based nano-materials.

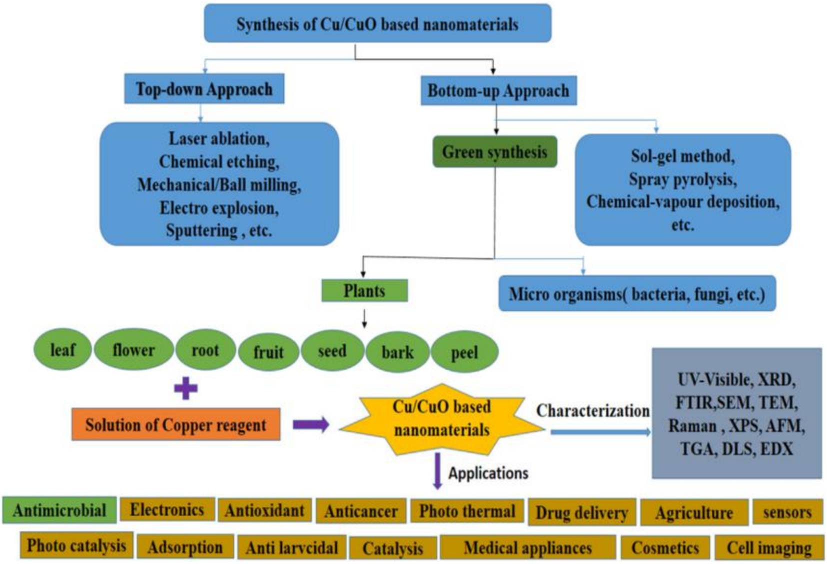


Fig 1: Flowchart representing the biosynthesis of Cu/CuO based nanomaterials

2. Biosynthesis of Cu/CuO based nanomaterials

Plants consists of large number of biologically active compounds and hence, most of the plants have proven record for their anthelmintic, antitumor, antimutagenic, antibacterial and fungicidal properties. The synthesis of metallic NPs involves simple mixing of metal solution with extract of plant. Nanoparticles are produced in the medium due to reduction of metal ions. The scheme of synthesis of metallic NPs is as shown in Figure 2.

2.1 Materials

Many earlier investigations revealed that Cu NPs can be synthesised by the application of most common precursor copper salts namely, cupric acetate (monohydrate) ($(CH_3COO)_2Cu \cdot H_2O$), Copper chloride di-hydrate ($CuCl_2 . 2H_2O$) and Copper sulfate pentahydrate ($CuSO_4.5H_2O$). Various factors such as concentration, pH, temperature, influence the nature and properties of synthetic Cu NPs as well as CuO NPs. The reduction of copper ions to get stable copper nanoparticles can be attributed to the presence of biologically active compounds present in the leaf broth of *Azadirachta indica* [13]. It was found in this study that the rate of production varied linearly with percentage of leaf broth. The other optimum conditions for the synthesis are; $[CuCl_2] = 7.5 \times 10^{-3}$ M, pH =6.6 and temperature = 85^{o}C.

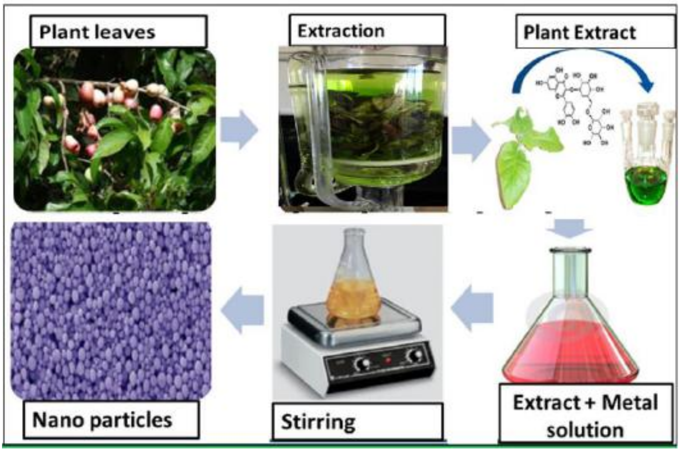


Fig 2: A schematic diagram of green synthesis of metal nanoparticles from plant extracts

2.2 Methods

The fresh/dried powder of plant parts is dispersed in distilled water. In the majority of cases, distilled water is used as the solvent. Now it is boiled at different temperatures according to the volatile nature of phytochemicals present in the plants, which can be accomplished through various extraction procedures. Now the extract is centrifuged and filtered out using a muslin cloth and Whatmann No. 1 filter paper. A particular volume of the filtered extract is measured out and is mixed with the precursor solution of particular volume and molarity [14]. A change in colour indicates the creation of nanoparticles, which is tracked using a UV–Visible spectrum. The overall flow chart for the synthesis of Cu/CuO-based nanoparticles is depicted in Figure. 1.

2.3 Green approach synthesis

Formation of greenly synthesized copper nano particles capped with *T. cordifolia* (Cu NPs@Tc) was also reported. Synthesis of Cu nanoparticles has been successful with extracts of various parts of plant species that include, *Citrus medica* Linn. (Idilimbu) juice, *Ziziphus spina-christi* (L.) Willd, *Asparagus adscendens* Roxb. Root and Leaf, *Eclipta prostrata* leaves, *Ginkgo biloba* Linn, *Plantago asiatica* leaf, *Thymus vulgaris* L, black tea leaves, *Terminalia catappa* leaf and many more presented in Table 1.

The organic hydrocarbon part of citron facilitates the protection of copper. The antioxidant nature and acidic property of citron also prevents oxidation of copper as the protons present in the medium influence electro-deposition of copper at low pH range. Cu colloid formation of non-oxidized Cu NPs was observed with uv-absorption peak at 565 nm during the green synthesis of Cu NPs by *Eclipta prostrata* leaves extract. The reduction of Cu^{2+} ions to Cu NPs by the phenolics and other chemicals of *Thymus vulgaris* L. leaf extract was reported. These biomolecules cogently reduce copper salts but also avoid agglomeration. The hydroxyl and ketonic groups of phenolic compounds bind to metals and show chelate effect. Flavonoids can directly scavenge molecular species of active oxygen. Antioxidant action of flavonoids resides mainly in their ability to donate electrons or hydrogen atoms. The reduction of copper ions to give Cu NPs was attributed to the phenolic compounds present in the *Rheum palmatum* L. root extract. The extract constituents believed to function both as reducing and capping agents in the stabilization of prepared Cu NPs.

The bioactive molecules present in the *Carica papaya* leaves extract also found to reduce precursor copper sulphate to form copper oxide nanoparticles. In the similar way CuO NPs were also synthesised by using plant extracts of Aloe vera, Oak fruit hull (Jaft), *Ixoro coccinea* leaf, *Syzygium alternifolium* (Wt.) Walp, *Ferulago angulata* (schlecht) boiss, *Rosa canina* fruit, *Azadirachta indica*, *Olea europaea* leaf extract, *Malus Domestica* leaf extract, *Bauhinia tomentosa* leaves extract, *Moringa oleifera* leaves Extract, *Abutilon indicum* leaf extract, *Eclipta prostrata* leaves extract, *Euphorbia Chamaesyce* leaf extract and many more as given in Table 1.

Table 1: Various plants extracts used in the synthesis of Cu and CuO NPs and their applications

Sr. No.	Plant	Image	Precursor	Size, morphology, surface plasmon vibration (SPV)	Applications	Ref
1	*Syzygium aromaticum* bud		Cupriacetate (monohydrate) ($(CH_3COO)_2Cu\cdot H_2O$)	-12 nm, spherical SPV@ ~580 nm	Antimicrobial properties	15
2	*Stachys lavandulifolia*		Copper chloride di-hydrate ($CuCl_{22}H_2O$)	80 ± 8 nm, near spherical, SPV@ ~ 590 nm	antibacterial activity	16
3	black bean		Coppersulfate pentahydrate ($CuSO_4.5H_2O$)	~26.6nm, spherical, hexagonal and uneven shapes,	anticancer activity	17
4	*Azadirachta indica* leaves		Cupric chloride di-hydrate ($CuCl_2.\ {}_2H_2O$)	48nm, cubical,SPV@ ~ 506 nm	-	18

5	*Tinospora cordifolia*		Copper chloride (CuCl$_2$(II))	50–130nm, spherical, SPV@~250 nm	Catalytic Degradation	19
6	*Citrus medica* Linn. (Idilimbu) juice		Copper sulphate (CuSO$_4$)	33nm, SPV@ ~ 631 nm	Antimicrobial activity	20
7	*Ziziphus spina-christi* (L.) Willd		Copper sulphate (CuSO$_4$)	8–15nm, spherical, SPV@ ~ 551 nm	Triphenylmethanedye and antibacterial assay	21
8	*Asparagus adscendens* Roxb. Root and Leaf		Copper sulphate (CuSO$_4$)	10–15 nm, Spherical, SPV@ ~ 500 to 700 nm	Antimicrobial Activities	22

9	*Eclipta prostrata* leaves		Copper acetate (Cu(OAc)2)	31±1.2nm, spherical hexagonal and cubical SPV@ ~ 565 nm	antioxidant and cytotoxic activities	23
10	*Ginkgo biloba* Linn		Copper chloride ($CuCl_2$)	15-20nm, spherical, SPV@560 to 580 nm	catalytic activity	24
11	*Plantago asiatica* leaf		Cupric chloride di-hydrate, ($CuCl_2\cdot {}_2H_2O$)	7–35nm, spherical, SP V@ 565 nm	catalytic activity	25
12	*Thymus vulgaris* L.		Copper sulphate ($CuSO_4$)	various sizes, sheeted, SPV @ ~ 520 nm	catalytic activity (MB)	26

13	Black tea leaves		Copper sulphate ($CuSO_4$)	26–40nm, Spherical,	antibacterial, antifungal aflatoxin B_1	27
14	*Terminalia catappa* leaf		Copper sulphate pentahydrate ($CuSO_4$ $5H_2O$)	21–30 nm, Spherical,	Antibacterial test	28
15	*Rheum palmatum* L.		Copper chloride ($CuCl_2$)	10–20 nm, Spherical, SPV@ ~ 250–300 nm	catalytic activity	29
15	Aloe vera extract		Copper sulphate $CuSO_4$	15 and 30 nm, dispersed, versatile and spherical, SPV@ ~ 265 and 285 nm	-	30
16	Oak Fruit Hull (Jaft)		Copper acetate ($Cu(CH_3COO)_2$)	34nm, quasi-s pherical, SPV@ ~ 590 nm	Photocatalytic Degradation (Violet 3)	31

17	*Ixoro coccinea* leaf		Copper sulphate $CuSO_4$	80–110 nm, Spherical, SPV@ ~ 191 nm	-	32
18	*Syzygium alternifolium* (Wt.) Walp.		Copper sulphate pentahydrate ($CuSO_4$ $5H_2O$)	17.5 nm, spherical, SPV@ ~ 285 nm	Antiviral Activity	33
19	*Ferulago angulata* (schlecht) boiss		Copper acetate ($Cu(CH_3COO)_2$)	~44nmSPV@~□554 nm	Photocatalyticdegradation of Rhodamine B	34
20	*Rosa canina* fruit		Cupric acetate, $Cu(OAc)_2$	Spherical15-25SPV@ ~ 262 nm	C-N Ullmann couplingreactions	35
21	*Azadirachta indica*		Copper nitrate Trihydrate ($Cu(NO_3)_2.3H_2O$)	28-35 nm, spherical SPV@~262nm	Antibacterial activity (E. coli)	36

22	*Olea europaea* leaf		Copper sulphate $CuSO_4$	20–50 nm, Spherical, SPV@ ~ 289 nm	toxicity activities	37
23	*Malus Domestica* leaf		Copper sulphate $CuSO_4$	18 - 20 nm, spherical and crystalline, SPV	antibacterial, antioxidant, DNA	38
24	*Bauhinia tomentosa* leaf		Copper sulphate $CuSO_4$	22-40nm, Clustered & spherical, SPV@ ~ 384 nm	antibacterial	39
25	*Moringa oleifera* Leaves		Copper sulphate pentahydrate ($CuSO_4 5H_2O$)	6 and 61 nm	Nitrates Removal	40
26	*Abutilon indicum* leaf		Copper(II) nitratetri hydrate ($Cu(NO_3)_2. 3H_2O$)	nm range agglomerated hexagonal wurtzite, SPV@ ~ 725nm	Antimicrobial, antioxidant and photocatalytic dye degradation activities	41

27	*Eclipta prostrata* leaves		Cupric acetate, Cu(OAc)$_2$	31±1.2nm, face-centered cubic structure, SPV@ ~565 nm	antioxidant and cytotoxic activities	42
28	*Calotropis procera*		Copper sulphate pentahydrate (CuSO$_4$ 5H$_2$O)	15–20 nm, quasi-spherical, SPV@ ~ 565 nm	adsorptive of Cr(VI)	43
29	*Euphorbia chamaesyce* leaf		Copper chloride (CuCl$_2$)	~ 36-40 face-centered cubic nm, Spherical (fcc), SPV@ ~ 325 nm	catalytic activity (4nitrophenol)	44

3. Formation mechanism for the synthesis of Cu/CuONPs from plant extracts

Green synthesis of CuONPs using plant extracts as the source of electron generation for the reduction of copper salt display some advantages over the use of microbes because it does not require cell culture maintenance and it can be scaled up for large-scale synthesis. The formation of CuONPs occurs with an observable change in the color of the extract when copper salt was added. Several studies have revealed that the phytochemicals in the plant extracts first form complexes with the iron salts and then reduce the ions to form nanoparticles. The biomolecules in the plants extracts usually react with copper ion to cause reduction which subsequently transform into CuONPs [41]. The probable mechanism involved in the synthesis of CuONPs is represented with the following equations.

$$\mathrm{Cu}^{2+} + \text{plant extract} \rightarrow [\mathrm{Cu}/\text{plant extract}]^{2+}$$

$$[\mathrm{Cu}/\text{plant extract}]^{2+} \xrightarrow{\text{heat}} [\mathrm{Cu(OH)_2}/\text{plant extract}]$$

$$[\mathrm{Cu(OH)_2}/\text{ Grass Extract}] \xrightarrow{\text{incubation}} \text{CuONPs}$$

4. Effect of reaction parameters on the biosynthesis of Cu/CuO nanomaterials

4.1 Effect of pH

pH value helps in the determination of the level of acidity and basicity on a solution. Report had shown the influence of varying pH value on the synthesis CuONPs and other metallic oxide nanoparticles. Significant influence of pH on size and texture of some nanoparticles biosynthesized from plant extracts have been reported. Also, variation of the pH value have been adopted in controlling the shape and size of the synthesized nanoparticles. Solution medium with pH values ranging from 7 to 9 has been considered as the optimum condition for the synthesis of nanoparticles from *Aeromonas hydrophila* extract [44].

4.2 Effect of type of plant extracts and concentrations

The synthesis of CuONPs using plants extract depend majorly on types of biomolecules found in plant extracts and the volume used. The volume of plant extracts used in the synthesis of nanoparticles influence the duration of synthesis. Previous study had shown that the higher volume of extract used, the faster the rate of synthesis because more chemical constituents are available in the solution which bind with the precursor to effect rapid bio-reduction and stabilization of nanoparticles. To attain an optimum condition for the green synthesis of CuONPs the ratio of the volume of plant extract must correspond to the concentration of copper precursor used. The yield of CuONPs depend largely on the volume of extract used for synthesis. Findings have proved that volume and kind of extract used for synthesis of nanoparticles have huge influence on their morphological properties and biological activities [45].

4.3 Effect Time

The incubation time of nanoparticles synthesized using plant extract has been examined to influence the morphological properties and qualities of nanoparticles. Other factors such as storage conditions and exposure to light also affect the reaction time of CuONPs. Long time incubation period has been stated to cause aggregation and shrinkage of particles [46].

4.4 Effect of temperature

Temperature have been considered as one of the crucial parameters that influences the synthesis of metallic oxide nanoparticles. The temperature recommended for the synthesis of CuONPs and other metallic oxide nanoparticles using plant extracts is in the range of 25–100 ^{0}C. However, the synthesis of CuONPs at room temperature is more rampant due to the volatility of some secondary metabolites found in plants extracts. The effect of temperature of reaction solution on the morphological identity of nanoparticles has been reported. Findings from the green synthesis of metallic oxides from plant extracts have shown rapid and complete synthesis at higher temperatures. However, higher temperature has been reported to cause poor synthesis of nanoparticles due to inactivation of biomolecules liable for the reduction of the iron precursor [47].

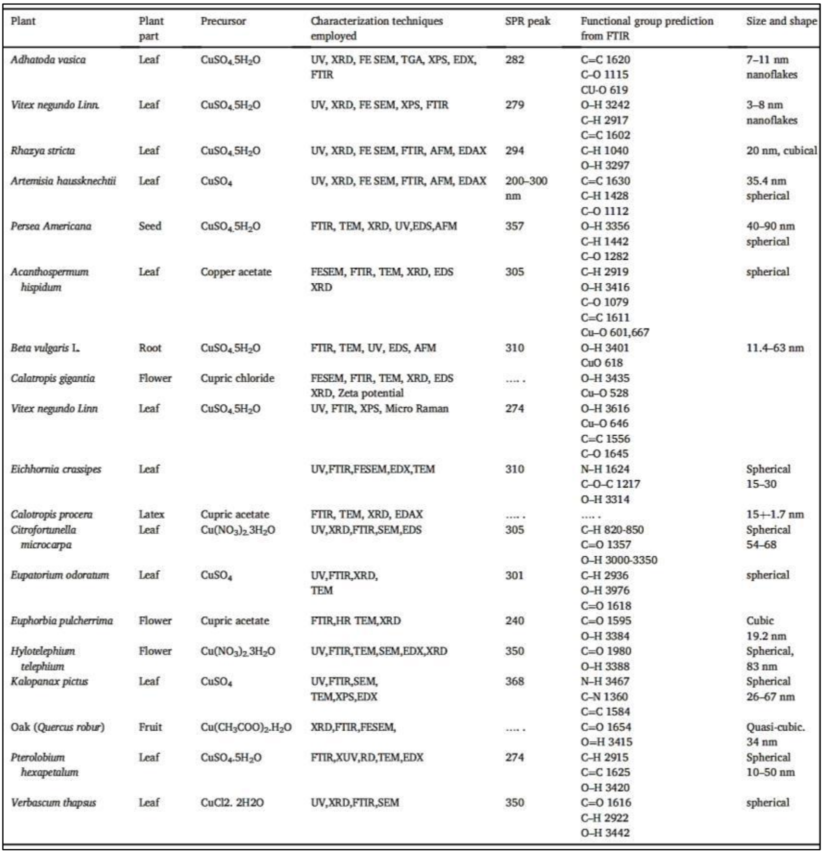
5. Characterization of Cu & CuO NPs

Since the applications of CuONPs depend largely on their properties, the need for their characterization therefore remain essential. The important characterization techniques used for determining the properties synthesized Cu & CuONPs are discussed below;

5.1 UV-visible (UV-Vis) spectroscopy

UV-visible spectroscopy is a molecular spectroscopy that is based on Bouguer Lambert Beer law principle for its operation. This technique measures the Plasmon resonance and total oscillations of conduction band of electrons in conjunction with electromagnetic waves. It is also used for absorption measurements of fluids and several other materials. In UV-visible spectroscopy analysis, a beam of light splits in two in which 50% of beams analysis the compound or solution in the transparent cell and the other 50% of the beam analysis the reference material parts. In the cause of the analysis, the solution absorbs light at a specific wavelengths, this wavelength is referred to as the surface plasmon resonance (SPR) of the material analyzed [48]. For CuONPs, the surface plasmon resonance is in the range of 200–350nm. Findings has demonstrated that the type of extract, pH, temperature and method of synthesis affect the SPR of CuONPs which further influence it morphological properties. UV-visible spectroscopy reveals crucial information about the size, structure, stability and aggregation of the CuONPs [49]. Findings on detailed application of UV as characterization tools in green synthesis of CuONPs are summarized in Table 2.

Table 2: Different characterization techniques employed in the plant-derived Cu/CuO based nanomaterials



Plant	Plant part	Precursor	Characterization techniques employed	SPR peak	Functional group prediction from FTIR	Size and shape
Adhatoda vasica	Leaf	$CuSO_4.5H_2O$	UV, XRD, FE SEM, TGA, XPS, EDX, FTIR	282	C=C 1620 C-O 1115 CU-O 619	7–11 nm nanoflakes
Vitex negundo Linn.	Leaf	$CuSO_4.5H_2O$	UV, XRD, FE SEM, XPS, FTIR	279	O–H 3242 C-H 2917 C=C 1602	3–8 nm nanoflakes
Rhazya stricta	Leaf	$CuSO_4.5H_2O$	UV, XRD, FE SEM, FTIR, AFM, EDAX	294	C-H 1040 O–H 3297	20 nm, cubical
Artemisia haussknechtii	Leaf	$CuSO_4$	UV, XRD, FE SEM, FTIR, AFM, EDAX	200–300 nm	C=C 1630 C-H 1428 C-O 1112	35.4 nm spherical
Persea Americana	Seed	$CuSO_4.5H_2O$	FTIR, TEM, XRD, UV,EDS,AFM	357	O–H 3356 C-H 1442 C-O 1282	40–90 nm spherical
Acanthospermum hispidum	Leaf	Copper acetate	FESEM, FTIR, TEM, XRD, EDS XRD	305	C-H 2919 O–H 3416 C-O 1079 C=C 1611 Cu–O 601,667	spherical
Beta vulgaris L.	Root	$CuSO_4.5H_2O$	FTIR, TEM, UV, EDS, AFM	310	O–H 3401 CuO 618	11.4–63 nm
Calatropis gigantia	Flower	Cupric chloride	FESEM, FTIR, TEM, XRD, EDS XRD, Zeta potential	.... .	O–H 3435 Cu–O 528	
Vitex negundo Linn	Leaf	$CuSO_4.5H_2O$	UV, FTIR, XPS, Micro Raman	274	O–H 3616 Cu–O 646 C=C 1556 C-O 1645	
Eichhornia crassipes	Leaf		UV,FTIR,FESEM,EDX,TEM	310	N-H 1624 C-O–C 1217 O–H 3314	Spherical 15–30
Calotropis procera	Latex	Cupric acetate	FTIR, TEM, XRD, EDAX	.... .	.... .	15+-1.7 nm
Citrofortunella microcarpa	Leaf	$Cu(NO_3)_2.3H_2O$	UV,XRD,FTIR,SEM,EDS	305	C-H 820-850 C=O 1357 O–H 3000-3350	Spherical 54–68
Eupatorium odoratum	Leaf	$CuSO_4$	UV,FTIR,XRD, TEM	301	C-H 2936 O–H 3976 C=O 1618	spherical
Euphorbia pulcherrima	Flower	Cupric acetate	FTIR,HR TEM,XRD	240	C=O 1595 O–H 3384	Cubic 19.2 nm
Hylotelephium telephium	Flower	$Cu(NO_3)_2.3H_2O$	UV,FTIR,TEM,SEM,EDX,XRD	350	C=O 1980 O–H 3388	Spherical, 83 nm
Kalopanax pictus	Leaf	$CuSO_4$	UV,FTIR,SEM, TEM,XPS,EDX	368	N-H 3467 C-N 1360 C=C 1584	Spherical 26–67 nm
Oak (*Quercus robur*)	Fruit	$Cu(CH_3COO)_2.H_2O$	XRD,FTIR,FESEM,	.... .	C=O 1654 O=H 3415	Quasi-cubic. 34 nm
Pterolobium hexapetalum	Leaf	$CuSO_4.5H_2O$	FTIR,XUV,RD,TEM,EDX	274	C-H 2915 C=C 1625 O–H 3420	Spherical 10–50 nm
Verbascum thapsus	Leaf	CuCl2. 2H2O	UV,XRD,FTIR,SEM	350	C=O 1616 C-H 2922 O–H 3442	spherical

5.2 FTIR spectrophotometer

FTIR spectrophotometer operates in long wavelengths in order to identify different functional groups associated with NPs. The FTIR spectral reveals functional groups present in extract containing NPs. At a specific resonant frequencies, the incident light from FTIR will cause an absorption when it come in contact with a vibration frequency of the group or bond corresponding to the same frequency. The shape of molecular potential energy, vibronic coupling and mass of an atoms are accountable for absorption of particular energy. The observed differences in the FTIR spectrum of different compound or molecule is traceable to the unique arrangement of atoms [50]. The peaks corresponding to O–H, C=O, C–N, C–H, C=C are the prominent peaks associated with CuONPs. Several scientific findings had ascribed the absorption at 3000–3350 cm^{-1} to N–H of amine or O–H of alcohol/phenol [51]. Absorption peaks in the range of 820–880 cm^{-1} have been attributed to aromatic C–H bending. A strong absorption peak at wavelength 2900-3000 cm^{-1} was credited to C–H. The absorption band observed at wavelength 1600–700 are traceable to CuO. The absorption band at 1600–1790 are linked to –C=O of carbonyl [53]. Reports on the comprehensive applications of FTIR in green synthesis of CuONPs are summarized in Table 2.

5.3 Size and morphological analysis

Size and morphological behavior are the most important parameters to investigate in nanoparticles because they influence the usefulness of CuONPs. The characterization equipment and techniques popularly used for size and morphology analysis are discussed as follows;

5.4 Scanning tunneling microscopy (STM)

This technique gives comprehensive information about the surface of CuONPs. It is used for size estimation, morphological study andtopography. It equally offers the advantages of wide range application for all forms of metals and semiconductor [53]. Quantum tunneling is the working principle guiding STM, Images are produced as variation of tunneling current tip causes movement across the surface. The growth of CuONPs has been measured with STM.

5.5 Atomic force microscopy (AFM)

AFM is used for the estimation of morphological properties such as size, roughness surface and texture. AFM is different from other electron microscopes techniques because it is only used for the 3D characterization of

NPs. It is capable of generating information about the geometry and magnetic behavior of nanoparticles. However, its scanning speed is slow compared to other microscopic techniques, it also produce in accurate topography especially when the probe is not dull [54]. Several morphological evaluation of biosynthesized CuONPs via AFM are showed in Table 2.

5.6 Transmission electron microscopy (TEM)

TEM is regarded as the best among other electron microscopy techniques for the determination of morphological identities of CuONPs and other metal nanoparticles. In TEM technique beams of energetic electrons are transmitted through an ultra-thin sample and interfaces from which a picture is shaped. The improved form of TEM with higher resolution that allows imaging of the crystallographic structure at nuclear scale is termed high resolution transmission electron microscopy (HRTEM) [55]. Reports obtained from the morphological evaluation of biosynthesized CuONPs using TEM and HRTEM are represented in Table 2.

5.7 Scanning electron microscopy (SEM)

SEM is used for morphological characterization of CuONPs. It is limited in some morphological analysis because it produces limited information regarding the true population and average size distribution. SEM has been reported to damage some nano-polymer. Therefore, for an effective morphological analysis using SEM, the NPs must be capable of withstand vacuum pressure [56]. Another retrogression about this technique is that it very expensive and slow. Other results showing the morphological characterization of biosynthesized CuONPs via SEM are represented in Table 2.

5.8 Dynamic light scattering (DLS)

DLS is sometimes referred to as quasi-elastic light scattering. It performs the function of size determination and aggregation of NPs [57]. This technique is very fast, sensitive and can estimate the size of a particle on both nano and macro scale but it also have some limitation because the size of an individual particle cannot be obtained from an aggregate. The speed of DLS is dependent on particle size; small particles are very as characterization tools in CuONPs biosynthesis are showed in Table 2.

5.9 X-Ray diffractometer (XRD)

XRD is used for structural and crystallinity analysis of synthesized CuONPs. X-ray diffraction analysis have revealed that CuONPs is a face-centered cubic phase in agreement with standard powder diffraction card

JCPD file No. 48–1548. The average crystallite size of CuONPs are estimated using Debye Scherrer formula.

$D = 0{:}9\lambda/\beta\cos\theta$

Where d = size of Cu-NPs (nm), λ = X-ray wavelength, β = full width at half maximum of the diffraction peak and θ = measured Bragg angle. The diffraction peaks at 2θ value of 31.6^0, $45.^04$, 56.4^0, 66.3^0 and 75.2^0that indexed planes (110), (112), (202), (220) and (004), respectively, was used to characterize the monoclinic structure of CuONPs [58]. Several findings on the structural and crystallinity analysis of biosynthesized CuONPs using XRD are represented in Table 2.

6. Applications of Cu/CuO nanomaterials

CuONPs synthesized using plant extracts have been reported to exhibit numerous applications in many fields. Some applications of CuONPs are discussed below as showed in Figure 3.

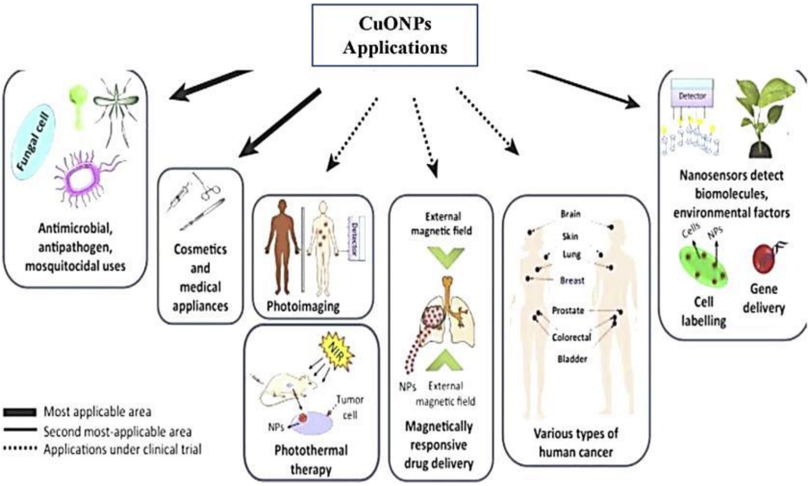
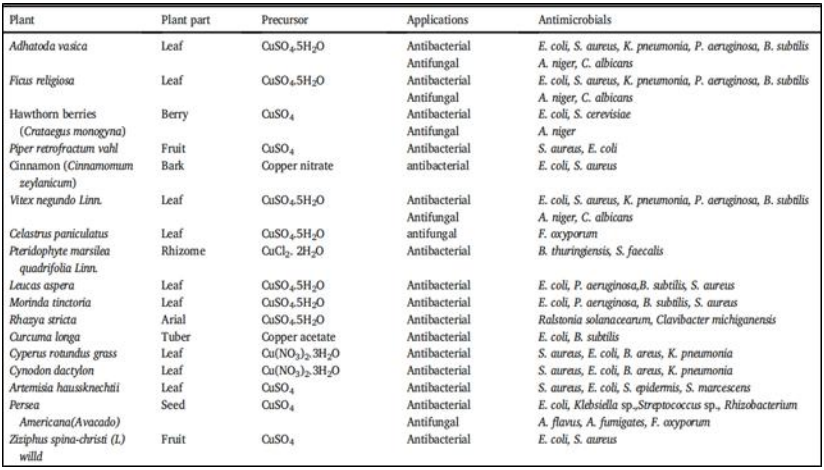


Fig 3: Flow chart showing some applications of CuONPs

6.1 Antibacterial application

The inhibitory antibacterial potential exhibited by biosynthesized CuONPs against both gram-positive and gram-negative bacterial strains had been studied. The antibacterial activities of phytosynthesized CuONPs from the extract of *Tecoma castanifolia* leaf displayed reliable bactericidal activity that may be useful in biomedical applications. Previous study have shown that the biomolecules of plant extracts used in CuONPs synthesis promote greater antibacterial efficacy against Gram-positive and Gram-negative bacterial strains. The increase in the antibacterial efficacy of CuONPs has been linked with the biomolecule (terpenoids) found in the extract during the capping process [59] The antibacterial analysis of CuONPs obtained from the agar well diffusion technique against both gram positive bacteria (*Streptococcus mutans* and *Staphylococcus aureus*) and gram negative (*Pseudomonas aeroginos, Klebsiella pneumonia* and *Escherichia coli*) showed the toxicity of CuONPs in destroying the growth of tested pathogens. The bactericidal effectiveness of CuONPs has been traced to the development of highly reactive oxygen species such as (OH, H_2O_2 and O^{2-}) on the surface of the CuONPs which causes the death to the bacteria. Reports on the antibacterial activities of CuONPs are summarized in Table 3.

Table 3: The antimicrobial activity shown by Cu/CuO nanomaterials derived from different plant extracts



Plant	Plant part	Precursor	Applications	Antimicrobials
Adhatoda vasica	Leaf	$CuSO_4.5H_2O$	Antibacterial Antifungal	*E. coli, S. aureus, K. pneumonia, P. aeruginosa, B. subtilis* *A. niger, C. albicans*
Ficus religiosa	Leaf	$CuSO_4.5H_2O$	Antibacterial Antifungal	*E. coli, S. aureus, K. pneumonia, P. aeruginosa, B. subtilis* *A. niger, C. albicans*
Hawthorn berries (*Crataegus monogyna*)	Berry	$CuSO_4$	Antibacterial Antifungal	*E. coli, S. cerevisiae* *A. niger*
Piper retrofractum vahl	Fruit	$CuSO_4$	Antibacterial	*S. aureus, E. coli*
Cinnamon (*Cinnamomum zeylanicum*)	Bark	Copper nitrate	antibacterial	*E. coli, S. aureus*
Vitex negundo Linn.	Leaf	$CuSO_4.5H_2O$	Antibacterial Antifungal	*E. coli, S. aureus, K. pneumonia, P. aeruginosa, B. subtilis* *A. niger, C. albicans*
Celastrus paniculatus	Leaf	$CuSO_4.5H_2O$	antifungal	*F. oxyporum*
Pteridophyte marsilea quadrifolia Linn.	Rhizome	$CuCl_2$. $2H_2O$	Antibacterial	*B. thuringiensis, S. faecalis*
Leucas aspera	Leaf	$CuSO_4.5H_2O$	Antibacterial	*E. coli, P. aeruginosa,B. subtilis, S. aureus*
Morinda tinctoria	Leaf	$CuSO_4.5H_2O$	Antibacterial	*E. coli, P. aeruginosa, B. subtilis, S. aureus*
Rhazya stricta	Arial	$CuSO_4.5H_2O$	Antibacterial	*Ralstonia solanacearum, Clavibacter michiganensis*
Curcuma longa	Tuber	Copper acetate	Antibacterial	*E. coli, B. subtilis*
Cyperus rotundus grass	Leaf	$Cu(NO_3)_2.3H_2O$	Antibacterial	*S. aureus, E. coli, B. areus, K. pneumonia*
Cynodon dactylon	Leaf	$Cu(NO_3)_2.3H_2O$	Antibacterial	*S. aureus, E. coli, B. areus, K. pneumonia*
Artemisia haussknechtii	Leaf	$CuSO_4$	Antibacterial	*S. aureus, E. coli, S. epidermis, S. marcescens*
Persea Americana(Avacado)	Seed	$CuSO_4$	Antibacterial Antifungal	*E. coli, Klebsiella* sp.,*Streptococcus* sp., *Rhizobacterium* *A. flavus, A. fumigates, F. oxyporum*
Ziziphus spina-christi (L.) willd	Fruit	$CuSO_4$	Antibacterial	*E. coli, S. aureus*

6.2 Probable mechanism for the toxicity of CuONPs against bacteria

The presence of CuO produces reactive oxygen species which interact with bacterial cell membrane to aid the penetration of CuONPs into the bacterial cell. The disturbances caused by CuONPs in the cell membrane of the bacterial causes some malfunctions in the bacterial cell which results into the inhibition of the growth of the bacterial species which might finally lead to their death. The smaller size of CuONPs (nanometer) compare to the pore size of bacterial cells (micrometer) allows the easy penetration of CuONPs into the cell membrane without any interference. The destruction of the bacterial membranes by CuONPs could be via production of reactive oxygen species and radicals or by direct cell damage since superoxide and hydroxyl radicals are produced by metal oxides (CuO) [60]. The abundance of carboxyl and amines groups on bacterial cell surface could possibly attract Cu^{2+} ions towards the cell [61]. Therefore, the probable antibacterial mechanism can be associated with gene toxicity, mechanical damage or oxidative injury. The probable antibacterial toxicity is showed in Figure 4.

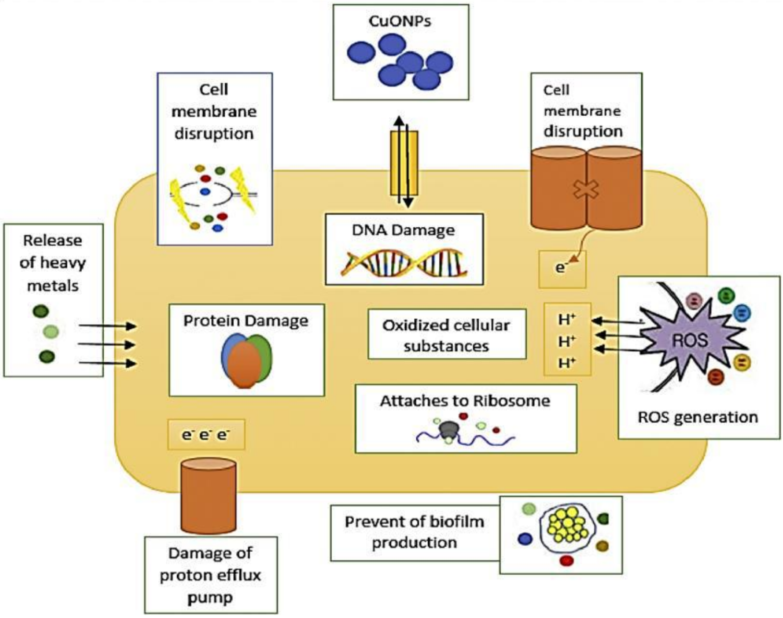


Fig 4: Probable mechanism of CuONPs toxicity against bacteria

6.3 Anticancer application

The anticancer investigation of CuONPs biosynthesized using the extract of black bean via the sulforhodamine-B assay revealed some alteration in the mitochondrial structure when incubated with CuONPs, the growth of cervical carcinoma cells were also greatly reduced when treated with CuONPs. Report have shown that CuONPs mediated from *Ficus religiosa* had potential anticancer efficiency against the growth of A549 adenocarcinomic human alveolar basal epithelial cells [62].

The recommendation of CuONPs in development and design of delivery carriers for cancer cell targeting due to demonstrated prominent toxicity accentuated as oxidative stress damage and DNA damage in cancer A549 lung cells has been made. The cytotoxicity of CuONPs mediated from the leaf extract of *Pterolobium hexapetalum* against human breast cancer cell line (MDA-MB-231) clearly showed enhanced effectiveness. Stating the importance of toxicity analysis in selecting nontoxic nanoparticles with distinctive biological activities, report on the *in vitro* toxicity investigation of phytosynthesized CuONPs reveals that they exhibit better toxicity efficacy that are beneficial in biomedical application when compared with chemically synthesized nanoparticles [63].

The report from the toxicity evaluation of CuONPs mediated from *Olea europaea* via animal model using 25 healthy male albino mice reveals that the CuONPs induces weight loss and exhibited dose-dependent toxicity. Several studies have shown the cytotoxicity of CuONPs against cancer cell growth [64]. Literature reports on the anticancer potency of CuONPs are summarized in Table 4, while the probable mechanisms of CuONPs induced cytotoxicity in cancer cell lines is presented with Figure 5.

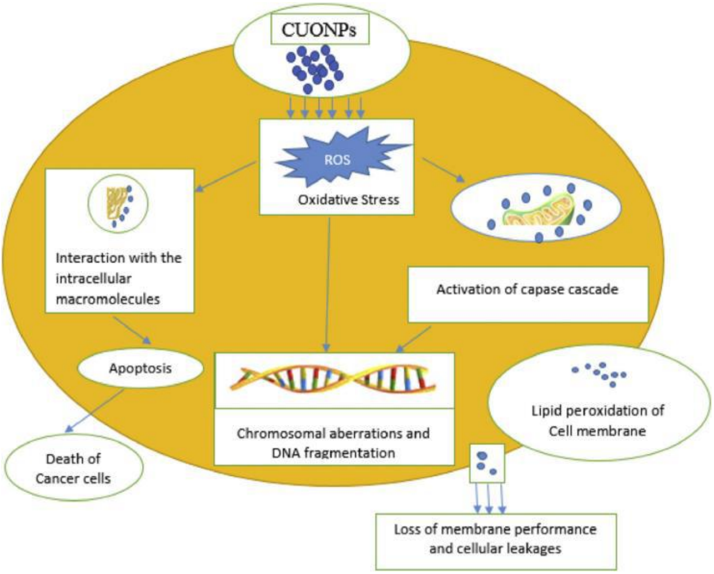


Fig 5: The probable mechanisms of CuONPs induced cytotoxicity in cancer cell lines

6.4 Catalytic application

Metallic and metal oxide nanoparticles has been reported to exhibit good photocatalytic efficiency. The photocatalytic degradation assessment of green synthesized CuONPs on RB dye revealed 94% degradation efficiency to the fifth cycle, which demonstrates the durability of the phytosynthesized CuONPs rendering it a good photocatalytic agent [65]. Furthermore, the comparative catalytic study of CuONPs and zinc oxide nanoparticles (ZnONPs) for basic violet 3 degradation indicated that ZnONPs exhibited higher catalytic activity than CuONPs. The degradation of basic violet 3 proceeded with pseudo-first-order kinetics. CuONPs synthesized using Thymus vulgaris leaf extract was reported as an outstandingly heterogeneous catalyst used in N-arylation of amines and indoles due to the remarkable percentage yield of N-arylated products obtained. The recovery and recycling of the catalyst for auxiliary catalytic reactions without ant loss in activity was also attained. The photocatalytic analysis of CuONPs mediated from Aloe Vera leaves under solar simulator light irradiation indicated that CuONPs completely degraded methylene blue in 10 min. This high activity is traceable to the phyto-constituents in Aloe Vera leaves [66]. More findings on the catalytic efficiency of CuONPs has been reported. The schematic representation of the degradation mechanism of CuONPs is showed in Figure 6.

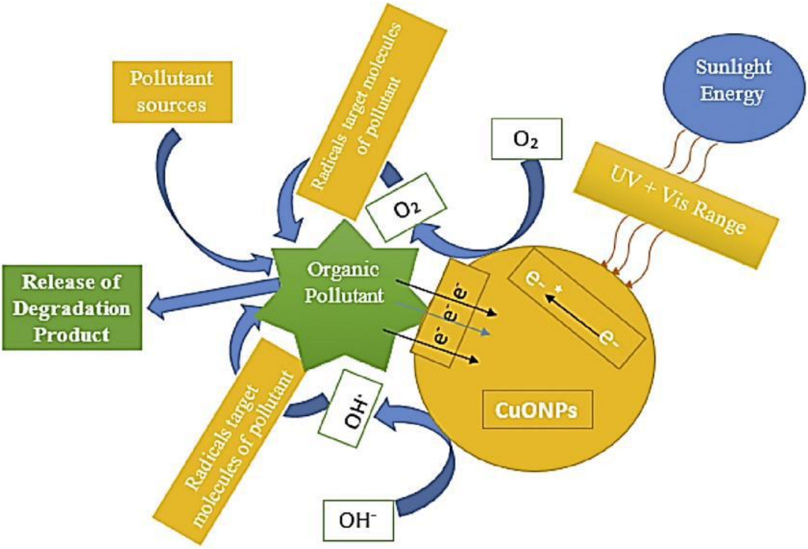


Fig 6: A schematic representation of degradation of some pollutants using the CuONPs

7. Conclusion

The method used in the synthesis of CuONPs predominantly affect the ecological identities as well as their physiochemical and morphological properties, which can influence their biological and catalytic applications. We discuss elaborately the biological method of synthesizing CuONPs from plant which offers great opportunity to medicinal institutes and other industries due to its biological activity and mode of synthesis.

The principal application of CuONPs in biomedical and waste treatment is attributed to their antimicrobial efficiency which depend largely on the morphological properties. The recent characterization techniques used in examining the identities of CuONPs are well highlighted. The efficiency of biosynthesized CuONPs as anticancer, antioxidant, antibacterial and effluent treatment has been properly discussed. The mechanism of synthesis and toxicity are well explicated. To improve the biological applications of CuONPs more research work should focus on possible route of minimizing CuO-NPs' toxicity while maintaining and improving their biological efficiency.

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Chapter - 5

Synthesis and Characterization of New Sm(III), Gd(III) and Ce(III) Complexes of (1E, 2E) Diphenylethane-1, 2-Hydrazone Oxime Ligand

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Chapter - 5

Synthesis and Characterization of New Sm(III), Gd(III) and Ce(III) Complexes of (1E, 2E) Diphenylethane-1, 2-Hydrazone Oxime Ligand

Vinay Singh and Gajanan Upadhye

Abstract

A simple and facile reaction of (1E, 2E)-1, 2-diphenylethane–1, 2-diene hydrazone oxime (HBMOH) with hydrated lanthanide (III) chlorides (where Ln = Sm, Gd and Ce) in 3:1 molar ratio in refluxing condition in presence of ethanol yielded the crystals of complexes. The microcrystals of the complexes are having red, green and yellow colored precipitate for Sm, Gd and Ce metal ions with HBMOH ligand respectively. The complexes were found to be stable at room temperature and characterized by the elemental analysis and spectrophotometric methods. Electrical properties and magnetic properties were also assessed. The spectral data were suggestive about surrounding of lanthanide metal ions with HBMOH ligand coordinated through the two nitrogen donor atoms of HBMOH ligand and nitrogen atom of monodentate chelating nitrito ligands.

Keyword: lanthanide (III) complexes, spectral techniques, elemental analyses, monodentate

1. Introduction

Studies in coordination compounds of lanthanides have revealed their applications and usefulness in varied arenas due to their characteristic 4f electrons. These 4f electrons imparted them with interesting physicochemical and influential magnetic properties [1-4]. Lanthanide complexes as liquid crystals have been also identified as anisotropic materials possessing remarkable photophysical properties [5, 6]. Lanthanide ions together with ligand can act as a probe for NMR shift and relaxation effect in aqueous solution and as contrast agent in the imaging of diseases by MRI technique [7, 8]. Lanthanide chelates have been applied in batteries, optical glasses, solar cells and other technological units [9-11]. It can also be applied as sensor for chiral biomolecules [12]. Lanthanide ions being small in size can substitute the other metal ions such as calcium present in the interior of the complex biomolecules like protein [13]. Hence, Lanthanide ions can also encounter the different kinds of calcium and potassium ions in neurons of living being [14]. Lanthanide ions particularly La(III) and Ce(III) are optimistic molecules for *in vitro* studies to assess the cytotoxic properties and anti-tumour activity [15].

Lanthanide (III) ions have multiple electronic energy levels on account of their electronic configurations [4]. Due to shielding of 4f orbitals, the lanthanide ions, except La(III) and Lu(III) ions, have characteristic *4f-4f* transitions [2]. But these transitions are Laporte forbidden offering lower probability for direct flipping of electrons hence, "antenna effect" which is essentially a ligand or linker is used to increase the efficiency of transition [1]. Eventually, allowed transitions had enhanced the charge-transfer luminescence property and this charger-transfer from excited state to ground state may happen due to M→LCT or L→MCT process. Also, size of lanthanide tripositive cations produce high coordination number, therefore well-coordinated geometry is observed when they coordinate with the ligands. Lanthanide ions, as per Pearson's HSAB theory, are hard lewis acids, therefore ligands having O-donor and N-donor atoms will tender ideal coordinating site for Lanthanides [16-18].

Schiff bases, a bidented ligand, having nirogen as donor atom and can be obtained from reaction between amine and carbonyl functionalities by nucleophilic addition following dehydration reaction [19]. Chelates of Schiff bases have been reported to exhibit wider applications in many sectors namely clinical, industrial, analytical etc. [20].

Henceforth, we had tried to design new metal chelates with Lanthanide tripositive cations and Schiff base in view of their potent applications. (1E, 2E)-1,2 diphenylethne-1,2-diene hydrazone oxime (HBMOH ligand) is such an Schiff base type of structure and play a flexible role in offering nitrogen as a donor atom. Here, we used greener and simpler route to prepare bidentated and unsymmetrical HBMOH ligand and their metal complexes with Sm (III), Gd(III) and Ce(III) metal ions. The synthesized coordination metal complexes were put under study for their electrical and magnetic properties. A plausible chemical structure for the complexes was also attempted on the basis of physical and chemical evidences.

2. Experimental

2.1 Materials and Instrumentation

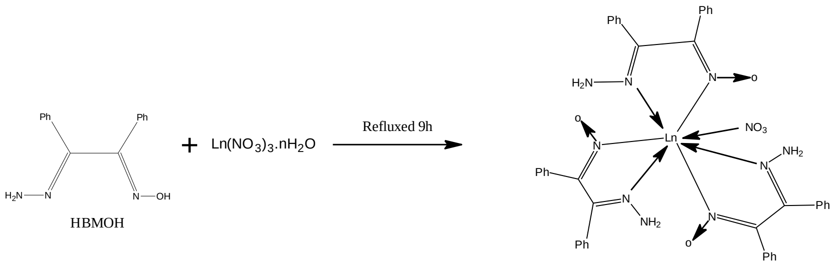
All manipulations were done in an aerobic environment. Organic molecules and lanthanide metal salts were acquired from SD Fine Chem. and employed without further purification. Melting points are uncorrected and are recorded on Gallen Kamp melting point apparatus. FTIR are recorded on Shimadzu Spectrophotometer using KBr disc. Magnetic properties are measured on Magnetic Susceptibility Balance Bruke Magnet B.M.6 at room temperature. Electrical conductivity is measured on Equiptronics conductometer.

2.2 Preparation of the HBMOH ligand [21]

2.25g (4.5 mmol) of hydrazine hydrate (80%) was added drop wise into 10g (4.4 mmol) of α–Benzilmonoxime with constant stirring. The resulting solution was kept stirring at room temperature overnight. The precipitated white crystals in ice cold water were separated and washed thoroughly with cold water. The residue was recrystallised from 60% ethanol and 8.13g (77%) of ligand was prepared and melting point was 172 °C.

2.3 Preparation of lanthanide (III) complexes

To a stirred ethanolic solution of hydrated lanthanide nitrate (1mmol), HBMOH (3mmol) was mixed and resulting solution of ligand and metal nitrate was subjected to reflux for 7-8 hours. As the reaction approached towards completion as monitored on TLC plates, the solution was left for evaporation at room temperature. Colored micro-crystals of complex were seen after two days of evaporation and it was separated by filtration. The micro-crystals were washed with cold ethanol and dried over calcium carbonate under vacuum. Observed yield was 70-75%.



Where Ln = Sm, Gd and Ce

3. Results and Discussion

The HBMOH powder, a bidentated and unsymmetrical ligand, and lanthanide metals in its nitrated salt form were mixed in allowed proportion of 3:1 to coordinate and produce respective metal complex. The binding nature and its type in the metal complexes were tentatively concluded by investigations and interpretations of PMR, physicochemical findings and their electronic absorption spectral scans. All three lanthanide metal (III) ion complexes here prepared were found stable and non-hygroscopic at room temperature. The sharp melting points had further added to the purity of the metal complexes. The analysis of constituent elements was in good agreement with the calculated percentages of elements. The values of electrical and magnetic properties of ligand and their metal complexes are as numbered in Table-1. Nitrobenzene was used as solvent while assessing the molar conductivities of ligand and complexes. It was measured in within the range of 23-25 $\Omega^{-1}cm^2mol^{-1}$ and this range of conductivity is parallel to conductivities of 1:1 electrolyte [22]. Unfortunately, attempts to get single crystal for obtaining x-ray diffraction data made us hopeless due to the low conductance values attributable to the coordination of the nitrate ion in these complexes.

Table 1: Analytical and physical data of the HBMOH ligand and its Ln(II) metal complexes

Compound	**Color**	**Yield %**	**M.P./Dec. Point ºC**	**Elemental Analysis**					**Magnetic Moments (B.M.)**	**Electrical Conductance 10^{-3} M (in DMF) mhos**
				% M Found (Calcd)	**% C Found (Calcd)**	**% H Found (Calcd)**	**% N Found (Calcd)**	**% O Found (Calcd)**		
HBMOH	Colorless	72.03	172	-	70.29 (70.27)	5.44 (5.32)	17.57 (17.58)	6.69 (6.75)	-	-
$[Sm(BMOH)_3]NO_3$	Red	70.00	245	16.71 (16.19)	56.01 (55.79)	4.00 (4.03)	14.00 (13.96)	5.33 (5.28)	1.53	23.00
$[Gd(BMOH)_3]NO_3$	Green	75.00	250	17.34 (17.22)	55.58 (55.12)	3.97 (3.88)	13.90 (13.83)	5.29 (5.21)	7.82	25.00
$[Ce(BMOH)_3]NO_3$	Yellow	74.35	248	15.75 (15.55)	56.65 (56.51)	4.05 (4.00)	14.16 (14.08)	5.40 (5.33)	2.78	23.00

3.1 Characterization of the complexes

3.1.1 FT(IR) spectra

The comparison of FTIR absorption peaks, in solid state (KBr), for free HBMOH ligand and synthesized lanthanide (III) complexes are as tabulated in the Table-2 and this assisted in predicting the coordination binding sites engaged in the chelate formation. The characteristic peak of HBMOH ligand at 3287 cm^{-1}, assigned to the vibrational frequency of the oximino -OH group, is absent in the FTIR spectra of Sm(III), Gd(III) and Ce(III) metal ion complexes. This can be inferred as participation of oximino nitrogen through the deprotonation of oximino group of free ligand to coordinate with the central lanthanide metal ions in solution state [23]. The peaks at 1647 and 1493 cm^{-1} in FTIR of free HBMOH was attributed to oximino and azomethine group respectively. The relevant peaks in the complexes were observed at lower frequencies suggesting the involvement of these groups in the chelation with core lanthanide metal ions [24, 25]. The appearance of new peaks in the region of 510-473 $cm^{-1}$with variable intensities in the spectra of complexes can be assigned to the stretching vibration of $Ln\rightarrow N$ and Ln-N [26, 27].

Table 2: FT(IR) spectral data for HBMOH and its Ln(III) metal complexes

Compound	υ(O-H)	υ(N-H)	Ar. C-H	C=NN	C=NO	N - O	N-N	M-N
HBMOH	3287	3387	3058	1647	1493	926	1072	-
$[Sm(BMOH)_3]NO_3$	-	3388	3059	1633	1441	1002	1088	491, 475
$[Gd(BMOH)_3]NO_3$	-	3383	3055	1631	1440	1000	1075	509, 503
$[Ce(BMOH)_3]NO_3$	-	3385	3060	1635	1443	1000	1075	510, 473

3.1.2 PMR spectra

The H^1 nmr recorded in deuterated DMSO solvent reflected the participation of proton of oximino group of HBMOH ligand via deprotonation where ligand itself acted as weak base to facilitate the deprotonation in situ [28] to coordinate with metal ion. In PMR, it is evident by the absence of peak for –OH group in the spectra of complex. The relevant data for other peaks is figured out in the Table-3. Complexes of both Sm(III) and Ce(III) had shown lower values of magnetic moments and this restricted the recording of PMR for both metal ion complexes.

Table 3: PMR spectral data for HBMOH and its Gd(III) complex

Compounds -OH $-NH_2$ N-H Phenyl ring
HBMOH 12.42 8.00 8.67 7.44-7.95 $[Gd(BMOH)_3].NO_3$ - 7.99 8.72 7.46-7.96

3.1.3 Electronic absorption spectra

In UV-Visible absorption spectrum of Free HBMOH ligand, the bands at 210 and 235 nm was thought to be due to the azomethine and oximino groups of ligand. The peak for *f-f* transitions in the Sm(III), Gd(III), and Ce(III) complexes are observed, though lanthanide ions are known to obscure the *f-f* transitions and their values are mentioned in Table-4.

The nature and extent of covalency between metal-ligand bond was assessed by calculating the other parameters like covalency factor ($b^{1/2}$), nephelauxetic ratio (β), and Sinha's covalency parameter ($\%\delta$). The nephelauxetic ratio is evaluated as ratio of $\nu_{complex}/\nu_{aquo}$. The value of β is used to calculate other parameters Sinha parameter in percentage as $\%\delta = [(1-\beta_{ave})/\beta_{ave}]\times 100$. The covalency factor ($b^{1/2}$) is provided by the expression, $b^{1/2} = [(1-\beta_{ave})/2]$ [29, 30].

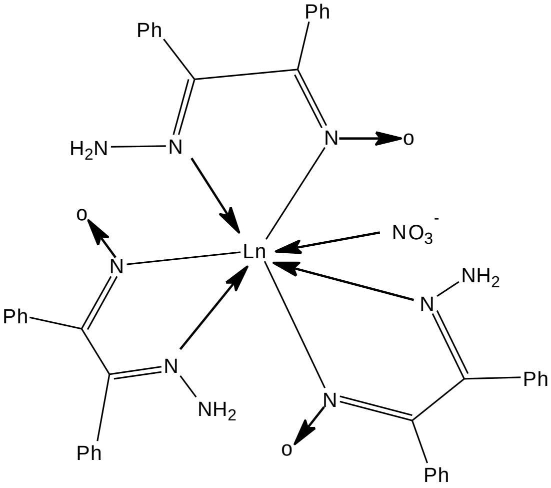
Calculated value of β parameter is less than unity whereas Sinha's covalency parameter ($\%\delta$) and covalency factor ($b^{1/2}$) are having positive values which asserts the involvement of *4f* orbital in the formation of lanthanide metal – ligand bond. Due to lanthanide contraction, the covalence of the Sm(III) complex is reduced [31].

Table 4: UV-Visible spectral data of HBMOH ligand and its Ln(III) metal complexes

Compound	**λnm**	**ε (dm³/mol/cm)**	**Transition**	
HBMOH	374	1499	$\pi^* \leftarrow \pi$	
	268	4670	$\pi^* \leftarrow \pi$	
	235	56688	$\pi^* \leftarrow \pi$	
$[Sm(BMOH)_3]NO_3$	883	45	$^4I_{9/2} \rightarrow {}^4F_{3/2}$	$\beta_{ave} = 0.9962$ $b^{1/2} = 0.04358$ $\delta\% = 0.4318$ $\eta = 0.0601$
	813	758	$^4I_{9/2} \rightarrow {}^4F_{5/2}, {}^2H_{9/2}$	
	583	987	$^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$	
	527	1325	$^4I_{9/2} \rightarrow {}^4G_{7/2}$	
	511	1987	$^4I_{9/2} \rightarrow {}^4G_{9/2}$	
$[Gd(BMOH)_3]NO_3$	565	996	$^8S_{7/2} \rightarrow {}^6P_{5/2}$	$\beta_{ave} = 0.9823$, $b^{1/2} = 0.0939$, $\delta\% = 1.80$, $\eta = 0.9458$
	410	4239	$^8S_{7/2} \rightarrow {}^6P_{7/2}$	
	385	8978	MLCT	
	255	11245	MLCT	
$[Ce(BMOH)_3]NO_3$	520	8795	$^5F_{5/2} \rightarrow {}^2D_{3/2}$	$\beta_{ave} = 0.9807$, $b^{1/2} = 0.0982$, $\delta\% = 0.0982$
	410	10256	$^5F_{5/2} \rightarrow {}^2D_{5/2}$	
	279	15987	MLCT	

4. Conclusion

Newer complexes in the series of HBMOH ligand with trivalent Sm, Gd and Ce had synthesized in the ratio of 1:3. The prepared complexes are stable enough to study their further properties. The interaction between metal and ligand was through *4f-4f* transitions. The HBMOH ligand, a Schiff base, acted as mono-negative ($[BMOH]^-$), bidented and unsymmetrical ligand. The HBMOH formed mononuclear complexes with tripositive lanthanide metal ions in good yields. It coordinated to metal ion with its oximino group at position six and one nitrate ion in lanthanide (III) nitrate complexes. The equilibrium geometry acquired by the complex can be possibly predicted as based on revealings from spectral data:



Where Ln = Sm, Gd, Ce

Additionally, X-ray crystallography is required to ensure the establishment of proposed structure for complexes synthesized and to assign the proper configuration.

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Chapter - 6

Chemistry of Batteries in Electric Mobility Solutions

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Chapter - 6

Chemistry of Batteries in Electric Mobility Solutions

Sajith Kumar Chandran

Abstract

The next generation of mobility solutions are heavily dependent on battery technologies rather than internal combustion engines (ICEs), which are driven by fossil fuels. The world is facing an unprecedented threat of global warming due to the uncontrolled emissions caused by burning of fossil fuels during the past century. The global effort to save the world is primarily based on switching the energy requirements from fossil fuels to renewable energy resources. Renewable energy resources are very poor in efficiency and therefore, the only alternative solution is employing electric power. For electric mobility solutions, highly efficient rechargeable batteries are essential. Such highly reliable battery technologies are intensely driven by chemistry, by several methodologies of converting chemical energy into electrical energy. The chapter discusses the chemistry behind various battery technologies which are available today for electric mobility solutions and the chemistry behind them.

Keywords: Batteries, electric vehicles, electrochemistry, energy density.

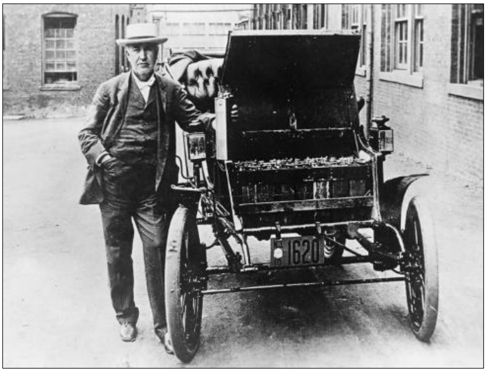
Introduction

Chemistry plays an important role in everyday life of mankind with innumerable products it develops to make life easier and comfortable. Any product, whether it's is life saving medicines, beautifying personal care products, luxurious fragrances, water purifying agents, pesticides to kill the weeds that affect food crops or a rope tied to a safety harness, a significant role is displayed by chemistry in all the products we experience today [1]. A major global concern of today is the alarming temperature rise in various parts of world due to global warming, which is expected to escalate the water levels of oceans, submerging many low-lying ports and cities to become non-existent in three to five decades. To mitigate this emergency, world has risen to reduce the carbon emissions by switching from fossil fuel burning to sustainable energy resources. Renewable energy resources are inherently low in efficiency even with the existing advance technologies [2]. There is a high demand for reliable and highly efficient sustainable solutions for the ever-increasing energy demands of the world. One of the green energy sources which is having the potential to sustain and support this high demand is electrical energy generation and storage from alternative efficient sources. There is a high global compulsion to reduce burning of petroleum products before we reach the alarming situations. This is only possible if we stop using automobiles, which are heavily dependent on fossil fuels, and, electricity generation based on coal combustion. However, this situation is going to affect the mobility of the world and therefore various automobile companies are switching to electrical mobility solutions as the need of the day. The present-day global fuel disruptions facilitated to accelerate this shift to electrical mobility solutions. The chemistry surrounding electrical energy storage and distribution has a large role to play to power electrical mobility solutions (electric vehicles-EV) with the modern engineering technologies that are emerging today. At the heart of this is the chemistry driving the rechargeable battery technology. The proceeding discussion focus on the electrochemistry of rechargeable batteries which are powering the electrical mobility solutions, the active materials used in the battery construction, the challenges and the way forward for sustainable solutions.

History of electric vehicles (EV)

As electricity is one of the sustainable energies, the concept of replacing internal combustion engines (ICE), which use petroleum fuel is very relevant. This introduced the idea of using electricity to power up the vehicles, the concept of an electric vehicle being introduced to the world in the year 1832. In the 1830s, Robert Anderson developed the first crude electric vehicle, but later in 1860s electric cars became more practical than before when the technology of rechargeable batteries came along in 1859, making the electric-car idea more practicable. Around 1884, Thomas Parker invented and deployed electric-powered trams and constructed prototype electric cars in England. In the year 1890, William Morrison, a chemist from Iowa claimed for a patent for the electric carriage he made in 1887. The popularity of electric vehicles did not last for long and it became less in demand in three decades. The decline in the popularity of electric vehicles (EVs) was due to the lengthy time required for the batteries to recharge, which is exactly like refilling the fuel tank. But the time required to recharge the batteries in the electric vehicles was longer, which was quite inconvenient to the electric vehicle users. However, due to the global oil shortage faced in 1970, the increased concerns of environmental pollution and awareness of air quality in 1980, the interest in electric vehicles once again resurfaced [3].

The first practical electric car built by the English inventor Thomas Parker in 1884 [4]



Thomas Edison poses with his first electric car, the Edison Baker, and one of its batteries [5]

Indian scenario

India is the fifth largest car market in the world and progressing towards one of the top three in the years to come. As per the statistics, only 4% of Indians have access to private mobility and this is going to increase many folds by 2030 as nearly 400 million people are looking forward for private mobility. In the coming decades, Indian roads will be burdened with more than 200 million cars, motorcycles, 3-wheelers, and trucks with the number of vehicles growing at the rate of 23%, which is behind China [6].

Electric mobility solutions

The biggest challenge for the automobile industry is to adopt quickly to the changing times, the demand it possesses in terms of reducing emissions and switching to more greener solutions. Over the years, the automobile and crude oil processing research and development companies invested heavily on emission reducing technologies like catalytic converters etc., but it has not helped to retard the alarming rise in pollution levels [7].

The present challenge is to reduce carbon emission on an unprecedented pace and that is only possible by switching to electric mobility solutions. Electric mobility uses rechargeable energy which is the electricity supplied by batteries. Electric mobility includes all the street vehicles using electric motor that rely on the electricity power either fully or partially. Vehicles using purely electric motor (Electric Vehicles-EV), vehicles using small combustion engine and electric motor (Range Extended Electric Vehicles-REEV) as well as vehicles using conventional internal combustion engine system and electric propulsion system (Hybrid Electric Vehicles-HEV) are considered as electric mobility [8].

The central part of electric mobility is the sources and technologies which can supply uninterrupted electric power for long hours. To obtain such portable power, the primary and reliable source is batteries which are rechargeable. Past few years, scientists across the world are developing and upgrading battery technology to meet the fast-growing demand.

The electric power drawn from batteries are based on chemical reactions which provide constant flowing of electrons, which is otherwise called as electricity. Though there are enough reactions that can provide release of electrons during the reactions, the success lies in effectively transporting these electrons over an external circuit or batteries that is primarily depend on various other factors. The conversion of chemical energy into electrical energy with the required physical parameters so as to use in mobility solutions is based on well-tailored chemistry and engineering methodologies. Initially, chemical energy to electrical energy conversion is made possible due to the chemical reaction taking place between the anode and cathode electrodes, the electrolyte or electrolytic solution [9]. This electricity drawn in such a manner could power up motors with sufficient torque, that are connected to electric powertrain systems, so as to carry the passenger and freight payload. Electric mobility (or e-Mobility) represents the concept of using electric powertrain technologies and connected infrastructures so as to enable the electric propulsion of vehicles and fleets. The term electric powertrain is often used to describe several powertrain configurations that utilize electrical energy to produce propulsive torque. It includes the main components that generate and deliver power to the road surface for fully electric, hybrid electric and plug-in hybrid electric vehicle applications [10]. Schematic diagram of a battery electric vehicle (BEV) is shown in figure-1.

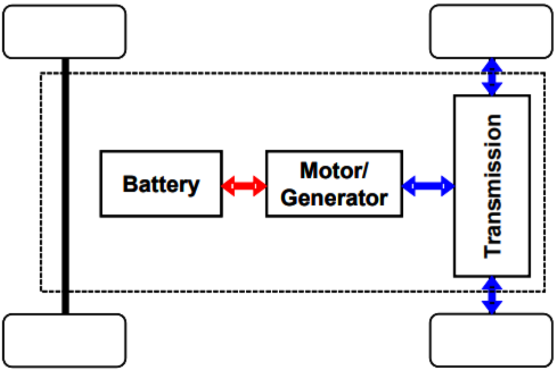


Fig 1: Schematic of a battery electric vehicle (BEV) powertrain [11]

Electric Vehicles (EV) or Battery Electric Vehicles (BEV)

Electric vehicles can be defined as all types of transport systems powered directly by electricity from micro mobility vehicles like electric scooters and pedal assisted e-bikes to fully powered 2- and 3-wheeled vehicles such as e-rickshaws and electric cargo bikes, and also very light 4-wheelers, cars and vans to trucks, buses, trolley buses, trams, trains, aircraft and ferries. These are vehicles which does not contain internal combustion engines (ICEs). Although there are alternative to conventional ICEs developed such as hybrid electric vehicles (cars, buses or trains) and hydrogen-powered Fuel Cell Electric Vehicles (FCEV), they are generally excluded from electric vehicles categories [12]. Electric vehicles use one or more electric motors to generate engine power, which is transferred to wheels for transportation. Presently, this type of mobility offers solutions for small trips and low weight (with bicycles, scooters and electric motorcycles) as well as long trips and heavy weight (electric public transport) vehicles. Electric vehicle technology is constantly evolving to make vehicles which are increasingly efficient and creating new uses for it like lorries, aircraft and electric boats etc though they are in experimental phase [13].

Traction battery

Traction battery, also called as electric vehicle battery (EVB), is one of the most important components of electric vehicles. Mainly buses, locomotives, industrial trucks and mechanical handling equipment use the traction batteries as power sources for mobility. These are specially designed rechargeable battery systems which are capable of providing long duration power to drive the powertrains. Schematic diagram of an electric vehicle wiring from battery is shown in figure-2. These batteries possess high capacity to weight and volume ratios, fast recharging capabilities, high energy density, ampere-hour capacity and sufficient working temperature range, but at the same time devoid of thermal runaways. In this manner they differ from SLI (Starting Lighting and Ignition) batteries, which are generally used for ignition and lighting purposes in conventional ICE automobiles. The traction batteries, unlike the SLI or auxiliary batteries, support all the functions of electric vehicles instead of just providing the energy needed to start the engine for the vehicles. These batteries are known as deep cycle batteries.

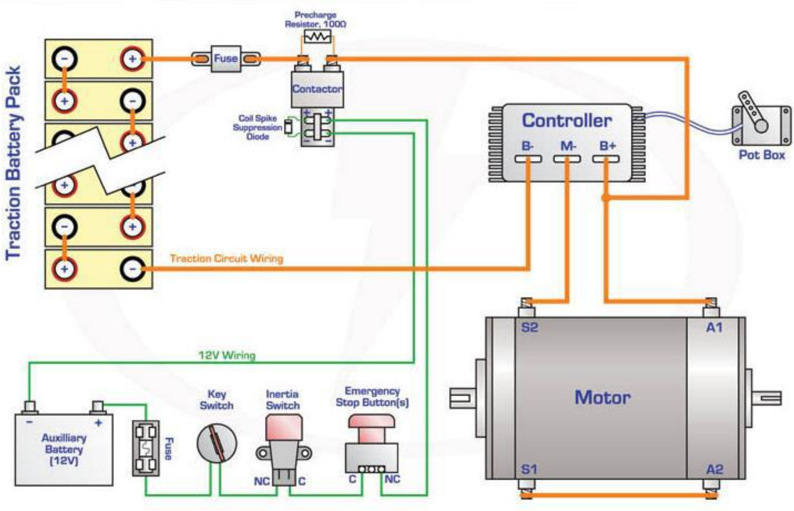


Fig 2: Schematic diagram of an electric vehicle wiring from battery [14]

Deep Cycle Batteries: Deep cycle batteries have the capability to discharge deeply and undergo several charging and discharging cycles, which is necessary for the electric vehicles' long life. This chemistry uses electrode which are thicker active plates, with higher-density active paste material and thicker separators. Alloys used as plates in a deep cycle battery varies in the chemical constituents than that of SLI batteries, mostly with larger content of antimony. Such thicker and alloy battery plates resist corrosion during extended charge and discharge cycles. These batteries can discharge 80% of power with consistent reliability [15].

Deep-cycle lead-acid batteries generally fall into two distinct categories; Flooded Lead Acid (FLA) and valve-regulated lead-acid (VRLA). These are otherwise known as sealed lead–acid battery (SLA). The FLA type of battery contains a quantity of electrolyte fluid so that the plates are completely submerged and hence termed as "flooded". The SLA is provided with a limited amount of electrolyte in the form of gel or electrolyte absorbed glass plate.

Electric mobility can be powered by various types of traction batteries such as lead-acid battery (flooded, deep cycle and VRLA), nickel-cadmium battery (Ni-Cd), nickel-metal hydride battery (NiMH), lithium-ion and lithium-ion polymer batteries. The types of rechargeable battery classifications which are generally employed in recent electric vehicles are shown in figure-3.

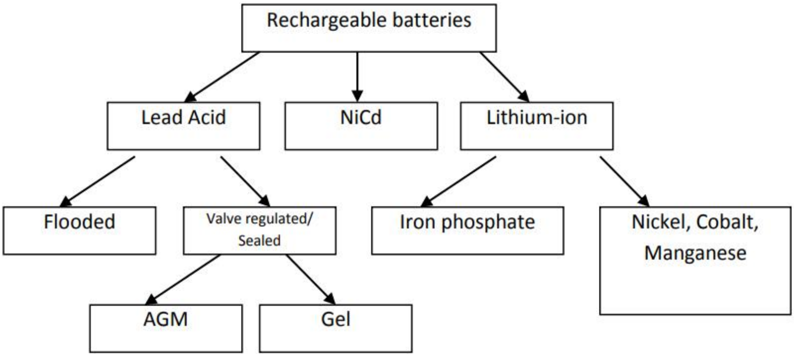


Fig 3: Classification of rechargeable batteries used in EVs [16]

Battery technologies

The use of batteries on various devices, instruments, machineries and electric mobility are depended on the active chemical material and the engineering intricacies. Apart from this, other parameters include energy density, number of charging and discharging cycles, the duration of uninterrupted power that can be drawn, deep cycle capability, durability or life of the internal components and cost effectiveness.

Battery is a device that converts chemical energy into electrical energy through a chemical reaction. The individual unit (basic electrochemical unit) containing an active material that participate in the reaction to release energy is known as “Cell”. The battery is array of such cells serially connected through an internal circuit. The various components of the battery are the active material which takes part in the charging and discharging reaction process, Electrode, the electrical conductor and the active materials undergoing the reaction, Electrolyte, the medium facilitating the transport of ions between the positive and negative electrodes, and Separators, which insulates the contact between the electrodes but allow movements of ions. The active material decides the characteristics and working parameter of various batteries. The electrodes are designated as positive and negative electrodes based of the type of reaction that occurs in the release of electrons. The chemical components of a battery are shown in figure-4.

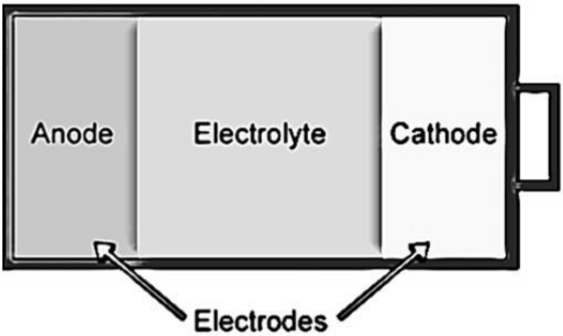


Fig 4: Basic Battery Chemistry [17]

Batteries are widely used in variety of devices and machinery; however, it is the complex chemistry occurring within the battery cells that enables to use them for various purposes, whether it is a battery for mobile, medical instruments, UPS systems, fork lift, machinery or electric vehicles. The convenience of using them in modern systems are based on the various chemistry involved during their functioning.

Batteries are composed of two terminals which are positive and negative terminals or cathode and anode, electrolyte and casing to hold all the components within. The electrolyte is added to divide anode and cathode but allowing the ions to flow. Battery undergoes an electrochemical reaction where the conversion of chemical energy to electrical energy occurs when a load or power supply is connected between the terminals. The evolution of the batteries can be arranged in the sequence of lead-acid battery, nickel-metal hydride battery, sodium-nickel chloride battery and a lithium-ion battery [18].

Lead-acid battery

The oldest battery technology, Lead-acid battery was invented in 1859 by Gaston Plante as the world's first rechargeable traction battery. This was the first type of rechargeable battery in the world that was commercially used especially in the industry of automobiles [19]. It was modified by Camille Alphonse Faure in 1881 and the performance and capacity of the modified lead-acid battery has improved by using the lead grid lattice [18-20].

Lead acid batteries are constructed with a number of individual cells containing layers of lead alloy plates immersed in an electrolyte solution, which is made of 35% sulphuric acid (H_2SO_4) solution (Figure 5). The plates are separated by an insulated separator. The lead dioxide plate function as positive electrode, while a metallic lead plate as negative electrode. Pure lead (Pb) is too soft and would not sustain the battery environment for long, so small quantities of other metals are added to provide mechanical strength and improve electrical properties.

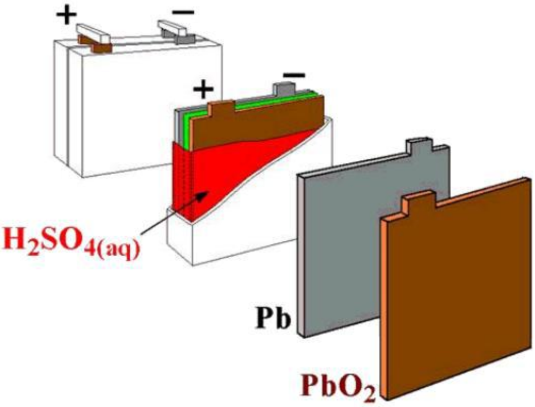
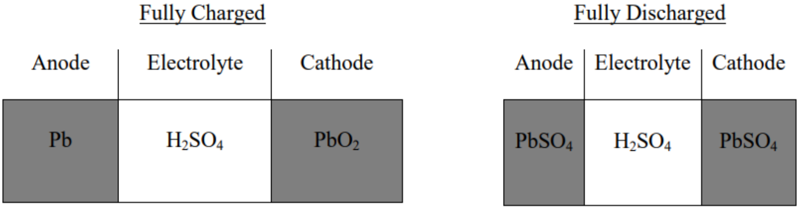


Fig 5: Schematic diagram of Lead-acid battery [21]

The most common type of metals that are added are antimony (Sb), calcium (Ca), tin (Sn) and selenium (Se). In each cell, both the plates are immersed in an electrolyte acid solution. As the electrodes are full immersed in the individual cell compartments, these are known as Flooded Lead Acid (FLA) batteries [8, 18].



Fully Charged

Anode	Electrolyte	Cathode
Pb	H_2SO_4	PbO_2

Fully Discharged

Anode	Electrolyte	Cathode
$PbSO_4$	H_2SO_4	$PbSO_4$

Fig 6: Lead acid battery compartments showing products of chemical reaction on charged and discharged conditions [16].

In the charge and discharge condition of lead acid battery, various chemical reactions take place for the conversion of energy, there by releasing electricity. The chemicals react together to release electrons, which result in electric current. The chemical reactions involved in the discharging and charging process is depicted in figure-6. Lead-acid batteries use lead dioxide (PbO_2) as positive electrode, a lead (Pb) negative electrode, and dilute sulfuric acid (H_2SO_4) electrolyte. When the battery discharges, the positive and negative electrodes turn into lead sulphate ($PbSO_4$), and the sulfuric acid turns into water. When the battery is charged, the opposite reaction occurs. In the fully charged state, 2V electric potential exists between the cathode and the anode.

Electrochemistry

The reactions involved in in the process is given below.

Discharge reaction

Reaction at the negative electrode

When a lead-acid battery is discharged after connecting a load such as a light bulb or a device between its positive and negative electrodes, the lead (Pb) in the negative electrode releases electrons (e–) to form lead ions (Pb^{2+}).

$Pb \rightarrow Pb^{+2} + 2e^-$

Then the lead ions immediately bond with sulphate ions (SO_4^{2-}) in the electrolyte to form lead sulphate ($PbSO_4$) and adhere to the surface of the negative electrode.

$Pb^{2+} + SO_4^{2-} \rightarrow PbSO_4$

Overall reaction at negative electrode

$Pb + SO_4^{2-} \rightarrow PbSO_4 + 2e^-$

Reaction at the positive electrode

Electrons (e^-) that have flowed from the negative electrode through the load to the positive electrode give the positive electrode a negative charge, attracting hydrogen ions (H^+) in the electrolyte. The hydrogen ions strip oxygen ions (O^{2-}) from the lead dioxide (PbO_2) in the positive electrode to form water (H_2O). Meanwhile, the lead dioxide from which the oxygen was stripped remains as lead ions (Pb^{2+}).

$PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O$

The lead ions immediately bond with sulphate ions (SO_4^{2-}) in the electrolyte to become lead sulphate ($PbSO_4$) and adhere to the surface of the positive electrode.

$Pb^{2+} + SO_4^{2-} \rightarrow PbSO_4$

Overall cell reaction

$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$

Charging Reactions

Reaction at the negative electrode

If a power supply is connected between a lead-acid battery's positive and negative electrodes during charging so that electrons (e^-) are forced to flow to the negative electrode, the lead sulphate ($PbSO_4$) that formed while the battery was discharging will revert to lead (Pb) in a reaction that releases sulphate ions (SO_4^{2-}).

$$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$$

Reaction at the positive electrode

Meanwhile, the positive electrode, from where electrons (e^-) were stripped, will gain a positive charge in a reaction in which water (H_2O) breaks down into oxygen (O_2) and hydrogen ions (H^+).

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$

Then, because the lead sulphate ($PbSO_4$) at the positive electrode lacks electrons, it will immediately react with oxygen to form lead dioxide (PbO_2) in a reaction that releases sulphate ions (SO_4^{2-}).

$$PbSO_4 + O_2 \rightarrow PbO_2 + SO_4^{2-} + 2e^-$$

The above activity at the positive electrode is summarized by

$$PbSO_4 + 2H_2O \rightarrow PbO_2 + SO_4^{2-} + 4H^+ + 2e^-$$

Overall charging reaction

$$PbSO_4 + 2H_2O \rightarrow Pb + PbO_2 + \underbrace{4H^+ + 2SO_4^{2-}}_{2H_2SO_4}$$

Compared to other battery designs, lead-acid batteries have a comparatively high self-discharge rate of 0.5% to 1% per day. They are also less capable to other battery formats in terms of energy density. Nevertheless, it will continue to be used in applications where energy density is not a primary consideration, like in SLI batteries. The other factors which affect the durability and working quality of lead-acid batteries are; electrolysis of water, reaction between electrodes and electrolyte, Impurities and chemical degradation by irreversible chemical reactions.

Another disadvantage of these batteries is the harmful effects of lead to humans and environment, though it has been almost eliminated by cent percent by recycling technologies which are available now. They have low capacity to weight and volume ratios and energy density.

Lead acid batteries are heavy and less durable than nickel (Ni) and lithium (Li) based systems when deep cycled or discharged (using most of their capacity). Lead acid batteries have a moderate life span and the charge retention is best among rechargeable batteries. These are safe batteries, which do not have the risk of fire and explosions.

Nickel Metal Hydride Batteries (NiMH)

Nickel-metal hydride batteries are systems in which hydrogen can be stored and released between the electrodes on a reaction process. Invented by Stanford Ovshinsky in 1986, these are closely related to nickel-cadmium (Ni-Cd) batteries, the difference being instead of cadmium, hydrogen is used as the active element at a hydrogen-absorbing negative electrode (anode). These are considered as an advanced version of Ni-Cd batteries. The electrodes are made from a metal hydride, usually alloys of lanthanum and rare earths that serve as a solid source of reduced hydrogen that can be oxidized to form protons. The electrolyte is alkaline potassium hydroxide which facilitates the hydrogen transfers without being retained or absorbed by itself. The cell voltage is approximately 1.2 V.

The negative electrode (anode) of the nickel-metal hydride battery is a hydrogen storage medium that releases the hydrogen on charging and discharging, and enables the electrochemical reaction to take place [22, 23]. The nickel hydroxide $Ni(OH)_2$ serves as the positive electrode in the cell system.

Electrochemistry

Metal hydride cell chemistry works on the capability of some metals to absorb large quantities of hydrogen. Like any cell reaction, oxidation and reduction take place at both electrodes through an electrolyte which consists of 30% by weight of alkaline potassium hydroxide (KOH) in water.

Charging

At positive electrode

During charging, oxidation take place in nickel hydroxide $Ni(OH)_2$ electrode. The hydroxyl ion reacts with nickel hydroxide $Ni(OH)_2$ to form nickel oxyhydroxide (NiOOH) and water.

$Ni(OH)_2 + OH^- \rightarrow NiO(OH) + H_2O + e^-$

At the negative electrode

At the negative electrode, the MH electrode, the hydrogen-absorbing alloy is reduced. During the course of the reaction, water dissociates and the hydrogen released reacts with metal to form metal hydride (MH).

$M + H_2O + e^- \rightarrow MH + OH^-$

Overall reaction

$Ni(OH)_2 + M \rightarrow NiO(OH) + MH$

Discharging

At the positive electrode

During the discharge process, nickel oxyhydroxide (NiOOH) combine with water to release electron with the formation of $Ni(OH)_2$ and hydroxyl ions.

$NiO(OH) + H_2O + e^- \rightarrow Ni(OH)_2 + OH^-$

At the negative electrode

The metal hydride reacts with hydroxyl ion get oxidised to metal releasing water molecule and electron.

$MH + OH^- \rightarrow M + H_2O + e^-$

The process of charging and discharging state of NiMH batteries are given in the figure-7.

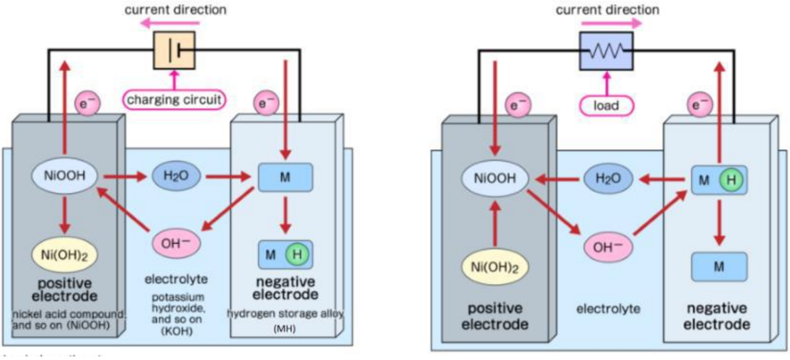


Fig 7: Charging and discharging state of NiMH batteries [24].

Ni-MH batteries find application in hybrid electric vehicles (HEVs), emerging EVs, and fuel cell EVs. In comparison to SLI batteries, NiMH batteries have higher power and energy density and a much longer life cycle. They are safer compared to Li-ion batteries, require less maintenance, fast and less expensive charging, low cost and environmentally more acceptable due to recyclability of materials [25-27]. Compared to SLA batteries, NiMH batteries have better capacity to weight and volume ratios and energy density.

The disadvantages of Ni-MH batteries include capacity deterioration upon cycling (due to corrosion) and high self-discharge as a result of active material decomposition and lower performance compared to lithium-ion batteries. They also suffer from memory effect (an unfavourable process where repeated partial discharge/charge cycles can cause a battery to 'remember' a lower capacity) and varying depth of discharge and lower state of charge. In addition, Ni-MH batteries require special sealed enclosures to prevent leakage of hydrogen [29]. The construction of NiMH cylindrical battery is shown in figure-8.

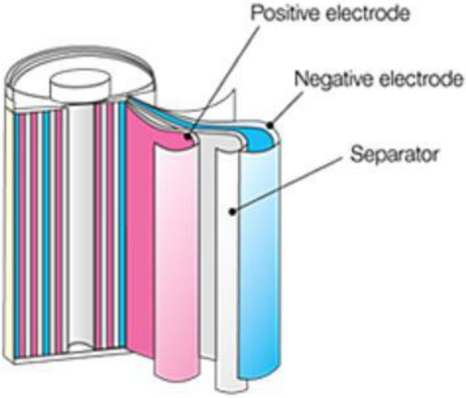


Fig 8: Schematic diagram of cylindrical NiMH battery construction [28].

The NiMH chemistry is still finding use in electric mobility for powering HEVs as it provides trouble free service for long years. These batteries are also capable of handling high power levels which in necessary in EV applications. They have safe operating temperature due to comparatively safer active chemicals and thus prevent the risk of thermal shoot ups, leading to explosions. Therefore, the EVs powered by NiMH does not require a very precise and robust battery management systems (BMS) [30].

Lithium-Ion battery

Lithium-ion batteries have revolutionized the energy storage technology and enabled the mobile and mobility revolution. Although Lithium metal was discovered by Johan August Arfwedson in 1817, the viability of using Lithium as battery material was unravelled only in mid of 1900. The Lithium-ion cell chemistry started in 1979 with the work of John B. Goodenough and his co-workers at Oxford University through their breakthrough discovery that Li_xCoO_2 with $0 < x < 1$ (lithium cobalt oxide/ lithium cobaltate / lithium cobaltite), another intercalated metal chalcogenide of type MX_2, could serve as a cathode material. John Goodenough, Stanley Whittingham and Akira Yoshino shared the Nobel Prize in Chemistry 2019, for the development of lithium-ion batteries. The modern rechargeable lithium-ion (Li-ion) batteries were developed and introduced in 1990s to the world with a significant weight advantage over other battery systems.

Lithium-ion battery, known to have one of the most outstanding qualities in the new electrochemical industry. It is one of the most widespread batteries used by electric vehicles today. The lithium-ion battery's weight advantages make it competitive with other battery systems. Because of its high specific energy, the lithium-ion battery has a relatively greater travel distance, which is about three times greater than that of lead acid battery. In the automotive industry, the lithium-ion battery has obvious advantages as it has a long cycle life, high energy capacity and high efficiency. These batteries are extremely likely to contribute more to the current market demands and the lives of people as the innovations, strategies and development of new products continues to advance [31-33].

Electrochemistry

With atomic number 3, lithium is the lightest metal with a density of only 0.53 g/cm^3. It also has a very low standard reduction potential (Li+/Li couple -3.05 V vs SHE), thus making it suitable for high density, high-voltage battery cells. However, lithium is a relatively reactive metal, which has to be protected from water, air and exotherms. So, needless to mention, they have to be fabricated with much higher safety measures [34].

The chemistry of Lithium-ion batteries is depended on intercalation process, a chemical process by which an ion is inserted or lodged into a host matrix with the retention of the crystal structure. During the charging and discharging process in Li-ion batteries, intercalation occurs in which lithium ions are incorporated into the structure of the electrode materials. Inside the cell, lithium ions move from the positive to the negative electrode during charging and from the negative to the positive electrode as the battery is discharged. The intercalation mechanism is shown in figure-9. The electrons released during the process move through an external circuit in the same direction as the lithium ions, driven by an external charger (when charging) or by the stored potential chemical energy (available to drive a load) when the battery is discharging.

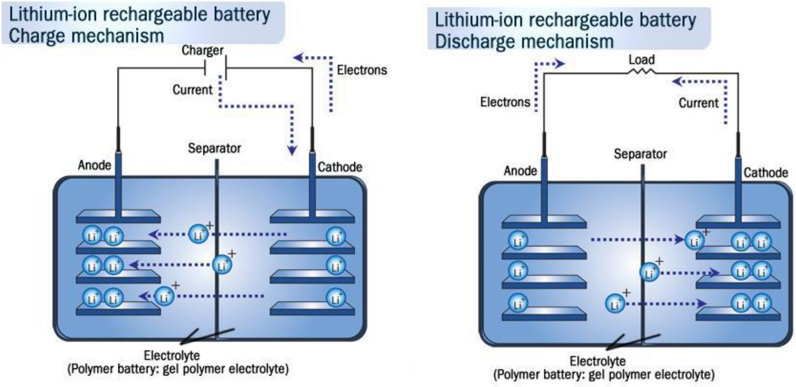


Fig 9: Intercalation mechanism during charging and discharging of Lithium-ion battery [35]

In a basic Li-ion battery cell, anode is lithium metal and cathode made up of TiS_2 (titanium disulphide), with $LiPF_6$ as the electrolyte in propylene carbonate as the solvent. A cell emf of approximately 2.5 V is obtained during the chemical reaction.

Reactions

Discharging

$Li \rightarrow e^- + Li_xTiS_2$

Charging

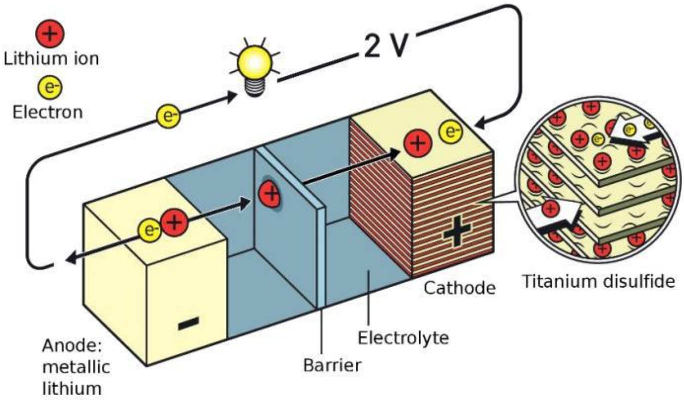
$Li_xTiS_2 + e^- \rightarrow Li$

Overall reaction

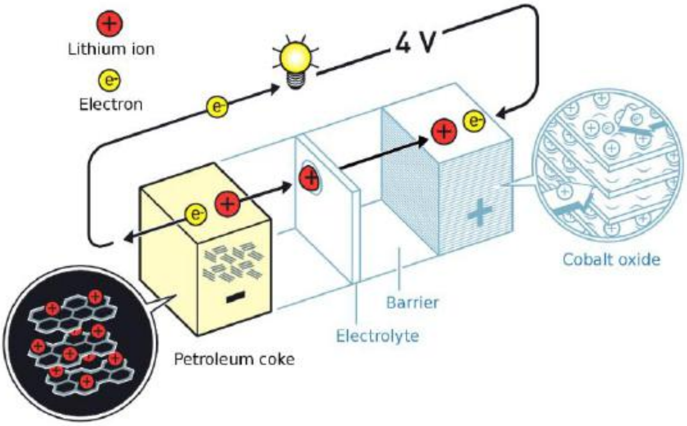
$xLi + TiS_2 \rightarrow Li_xTiS_2$

During the discharge, the reaction is proceeded by intercalation of the lithium ions into the titanium disulphide lattice and during the charging process, the lithiated $LiTiS_2$ electrode shows complete reversibility by pushing the Li ion back to the anode surface. Schematic diagram of the electrodes and electron transfer in Li-ion battery is shown in figure-10.

In modern day Li-ion batteries, a number of anodic and cathodic materials are used to enhance efficiency, facilitate better fabrication and operational versatility. They have a long-life cycle, comparatively low maintenance and do not suffer from the high self-discharge rate and memory effect, which is common in nickel-cadmium (NiCd) and nickel metal hydride (NiMH) batteries. Charging efficiency is as high as 99% in Li-ion chemistry. Unlike sealed lead acid (SLA) and NiCd, Li-ion batteries, Li-ion batteries do not contain toxic heavy metals, which causes environmental pollution and health risks. The construction of cylindrical and pouch type Lithium-ion cell is given in figure-11.



Lithium-based battery using Li_xTiS_2 as the cathode.



Modern commercial Li-ion battery using Coke based anode and Li_xCoO_2 cathode

Fig 10: Schematic diagram of the electrodes and electron transfer in Li-ion battery [36]

They have one of the highest energy densities (amount of energy a battery contains compared to its weight or size) of any battery technology today. This could drastically reduce the size and weight of batteries which are used in hand held devices. Li-ion battery cells can deliver up to 3.6 V, 3 times higher than other battery technologies such as NiCd or NiMH. The charge density profile of the batteries are given in figure-12.

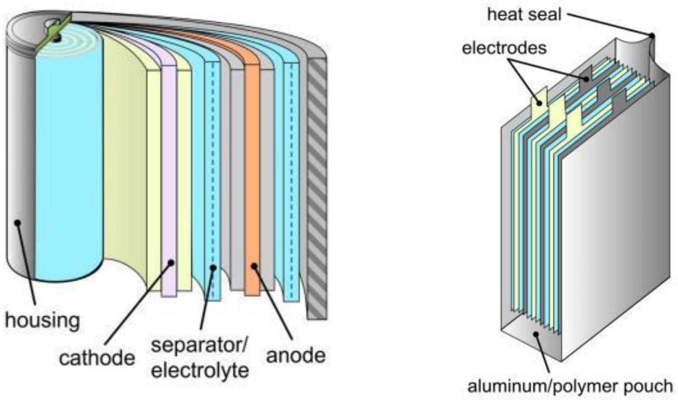


Fig 11: Lithium-ion cell construction [37]

Lithium-ion batteries can be fabricated in various format suitable to the usage. They offer excellent capacity to weight and volume ratios, state of charge and energy density. At the same time, Li-ion batteries are prone to fire and explosion and therefore, require robust battery management system.

Chemistry and EV battery safety

A major issue associated with EV batteries are the risk of heating, fire and explosion. This increases many folds with Li-ion batteries. The safety risks are a major concern for using them in electric vehicles as many incidents are reported world over. Ideally, to mitigate risks, the EV batteries should have a large range of working temperature, very sensitive battery management system, less reactive active chemicals which have lower flash point and explosion risks and excellent cooling systems for heat dissipation. The fire and explosion attributed to the batteries are due to their high energy content of active chemicals and energy storage capacity, heating during the electrochemical reactions, their closely compact and enclosed containers, electric and electronic short-circuits, over charging or subjecting the batteries to recharge or work beyond the recommended temperature ranges, which then leads to runaway reactions. Runaway reactions are those reactions which cannot be controlled when once triggered. The energy density profile diagram (figure-12) depicts why the safety risks increases while switching from lead acid batteries to Ni-MH and Li-ion batteries. Lithium metal is highly reactive and possess high energy. Moreover, the lithium batteries develop spikes which results in short circuit of cells. Major measures are to be adopted to circumvent this scenario, by adopting efficient thermal cut-offs, safety vents and incredible cooling systems. By using various safe active electrode materials can also bring down the risks, which is shown in figure-13.

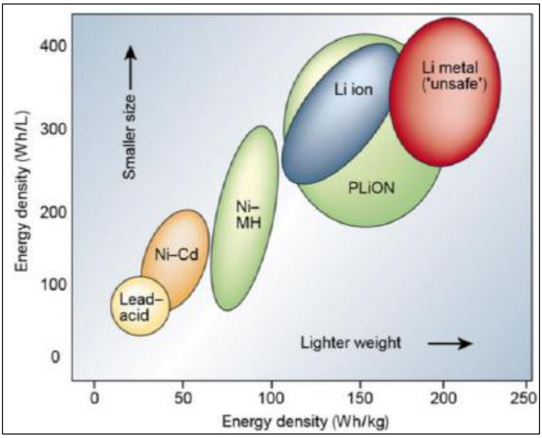
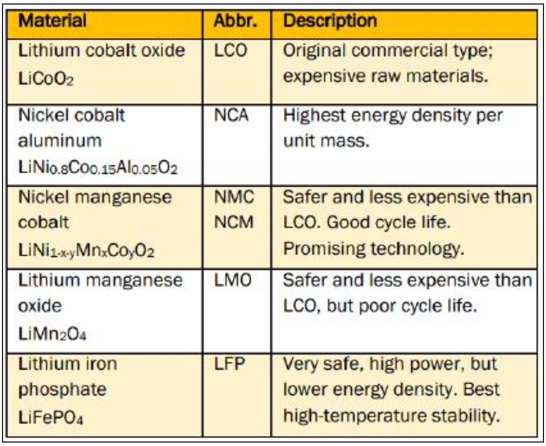


Fig 12: Energy density profile of batteries [38]



Material	Abbr.	Description
Lithium cobalt oxide $LiCoO_2$	LCO	Original commercial type; expensive raw materials.
Nickel cobalt aluminum $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$	NCA	Highest energy density per unit mass.
Nickel manganese cobalt $LiNi_{1-x-y}Mn_xCo_yO_2$	NMC NCM	Safer and less expensive than LCO. Good cycle life. Promising technology.
Lithium manganese oxide $LiMn_2O_4$	LMO	Safer and less expensive than LCO, but poor cycle life.
Lithium iron phosphate $LiFePO_4$	LFP	Very safe, high power, but lower energy density. Best high-temperature stability.

Fig 13: Some common positive electrode materials [39]

End of Life (EOL) of batteries

Another issue the world might encounter in future will be the pollution caused due to the discarded batteries. The lead acid batteries, after EoL can cause serious toxic and heavy metal pollution to environment. Though, we have very efficient recycle chemistry, how efficiently and completely this could be achieved is a challenge. The same situation might emerge with NiMH batteries too, as the recycle technologies are to be fool proof through education of masses and conscious buy back policies of battery manufacturers. Recycle and reuse can be the ways for batteries that reach their end of life cycle (EoL), which will give a big hand on reducing impact on environmental pollution. Besides that, the efficiency and lifespan of the batteries are to be invented with thorough research. Otherwise, mitigating pollution of carbon emission will lead to another dangerous situation to be solved in near future [40, 41].

Conclusion

Use of batteries in electric mobility is constantly evolving in terms of chemistry and engineering technology. As we move more towards lower carbon emissions and sustainable mobility, the battery technology has a lot to offer. Newer methods are to be designed to have more safe and efficient working of the batteries. All the above types of batteries have its own drawbacks in terms of air pollution at the cost of environmental pollution as more and more scrap batteries pile up. Though there are technologies developed to recycle the active materials and battery components, the scale up and maximum utilisation will be of great significance.

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Chapter - 7

Nanotechnology: A Recent Novel Tool in Pest Management

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Chapter - 7

Nanotechnology: A Recent Novel Tool in Pest Management

Manoj Kumar Jena, Prajapati Maulikkumar Rameshbhai, Kyada Amitkumar Dilipbhai and Satikanta Sahoo

Abstract

The chemical pesticides are used for managing the pest population on a large scale due to their sudden action. However, the continuous use of chemical pesticides in crop protection deteriorates soil health, water bodies and affects human health. It also lead to the rise in pest resurgence, resistance as well as secondary pest outbreak due to destruction of natural enemies. It has now become a global problem and a matter of serious concern. Therefore, more reliable and advanced methods are urgently required for the control of pests. Nanotechnology, an interdisciplinary field, has revolutionized different sectors of science and technology by introducing nanoparticles. Nanoparticles can be utilized for enhancing the efficacy of pesticides in reduced doses along with diminishing the environmental contamination. It also reduces the cost of management of pests. The use of nanotechnology in agriculture is less frequent compared to sectors like medicine and pharmacy. The various application of nanotechnology in managing pests, classes, biosynthesis as well as mode of action of nanoparticles are briefly discussed in this chapter.

Keywords: Nanotechnology, nanoparticles, nanopesticides, biosynthesis, pests

Introduction

Nanotechnology is one of the most promising new technologies in the recent decade and an interdisciplinary field having enormous potential in different areas such as medicine, pharmaceutical and agriculture. The term "nano" is derived from the Greek word meaning "dwarf". The term "Nanotechnology" was first used by Norio Taniguchi in 1947 (EPA, 2007). The word nanotechnology was evolved due to the use of particles with size ranging in nanometers (1 to 100 nm) (Bhattacharyya *et al.* 2010). Joseph and Morrison (2006) defined "Nanotechnology as the manipulation or self-assembly of individual atoms, molecules or molecular clusters into structures to create materials devices with new or vastly different properties”. It is one of the most reliable and expanding technologies of the 21st century. It has enormous advantages, especially in the field of agriculture, which include insect pest management through the formulations of nanomaterials based pesticides, development of insect pest resistant crop varieties and increase in agricultural productivity using bio-conjugated nanoparticles (Dimetry and Hussein, 2016). Nanoparticles have distinct physical, biological and chemical properties associated with extraordinary strength, high electrical conductivity and more chemical reactivity and chemical properties associated with their atomic strength (Leiderer and Dekorsy, 2008).

Applications of Nanotechnology in the Developing Countries

Sl. No.	Applications	Examples
1.	Energy storage and production	Carbon Nanotube (CNT) storage of Hydrogen and conversion
2.	Agricultural productivity	Herbicide delivery enhancement
3.	Water treatment and remediation	Nano-membranes
4.	Disease diagnosis and screening	Lab-on-Chip
5.	Drug delivery systems	Nano-capsules
6.	Food processing and storage	Coating/packaging
7.	Air pollution and remediation	Nano-catalysts
8.	Construction	Durability
9.	Health monitoring	Sensors
10.	Vector and pest detection/control	Sensors and pesticides

(Salamanca-Buentello *et al.* 2005)

Application of Nanotechnology in Pest Management

A. Pesticide delivery		
Chemical		
Avermectin	Porous hollow silica (15 nm)	Li *et al.* 2007
Ethiprole or Phenylpyrazole	Poly-caprolactone (135 nm)	Boehm *et al.* 2003
Gamma cyhalothrin	Solid lipid (300 nm)	Frederiksen *et al.* 2003

Tebuconazole/Chlorothalonil	Polyvinylpyridine and polyvinylpyridine-co-styrene (100 nm)	Liu *et al*. 2001
Biopesticides		
Plant origin: nanosilica for insect control	Nanosilica (3-5 nm)	Barik *et al*. 2008
Artemisia arborescens, Essential oil encapsulation	Solid lipid (200-294 nm)	Lai *et al*. 2006
Microganisms: *Lagenidium giganteum* cells in emulsion	Silica (7-14 nm)	Vandergheynst *et al*. 2007
Microbial product: absorption of *Myrothrecium verrucaria* enzyme	Chitosan/Kaolin (250-350 nm)	Ghormade *et al.* 2011
B. Pesticide sensor		
Carbofuran /Triazophos	Gold (40 nm)	Guo *et al*. 2009
DDT	Gold (30 nm)	Lisa *et al*. 2009
Dimethoate	Iron oxide (30 nm), zirconium oxide (31.5 nm)	Gan *et al*. 2010
Organophosphate	Zirconium oxide (50 nm)	Wang *et al*. 2009
Paraoxon	Silica (100-500 nm) Carbon nanotubes	Ramanathan *et al.* 2009, Joshi *et al.* 2005
Pyrethroid	Iron oxide (22 nm)	Kaushik *et al*. 2009
Pesticide degradation Lindane	Iron sulude (200 nm)	Paknikar *et al*. 2005
Imidacloprid	Titanium oxide (30 nm)	Guan *et al*. 2008

Role of Naturally Occurring Nanoparticles in Insects

The naturally occurring nanoparticles are seen from different parts of the body, including the compound eyes, antenna, wings and abdomen, that isolated nanoparticles of abdomen and antennae have diameters of about 12 and 11 nm, respectively. These include ordered hexagonal array of structures in wings of cicada, *Psaltoda claripennis* (Ashton) and termite of the family Rhinotermitidae (Zhang *et al*. 2006). The size of these nanoparticles varies from 200 to 1000 nm. These wing structures have a round shape at the top and there is a protrusion of about 150 to 350 nm on the outer side. These features increase the aerodynamic efficiency of the insect. The bright coloured components present in butterfly wings are also nanoparticles. These naturally occurring nanoparticles have been reported to be responsible for plant-insect interactions (Gorb and Gorb, 2009). Spider silk is also nanoparticle. Silk is the material known with about five times higher strength that of steel of the same weight. The remarkable characteristics of spider silk are because of the proteins that build the silk (mainly fibroin) and its supramolecular organization which is at the nanoscale level (Filipponi *et al*. 2010). The honeybees, ants *Formica rufa* (Linnaeus) and *Solenopsis invicta* (Buren) used the geomagnetic field information for foraging, homing and orientation (Slowik *et al*. 1997; Binhi, 2004). The magnetic signals in ant species has been recognized by using magnetite nanopartilces which is observed by electron microscope. In the abdomen of workers *S. Invicta*, the ferric ions has also been observed (Abracado *et al*. 2005). Magnetic elements have been detected in the European honeybees *Apis mellifera* (Linnaeus), ants *Pachycondyla marginata* (Roger), stingless bees *Schwarziana quadripunctata* (Lepeletier) (Wajnberg *et al*. 2000; ElJaick *et al*. 2007; Sahoo, 2014). To detect the natural magnetism in the fire ant *S. invicta* of workers and queens by using the Magnetic resonance imaging (MRI). Some ferromagnetic material is found in different body parts of some insects which are magnetic nanoparticles and act as geomagnetic sensors specifically in social insects (Esquivel, 2007). The insecticidal properties of polyethylene-glycol-coated nanoparticles, which is responsible for almost 80 percent mortality in *Tribolium castaneum*, is due to continuous release of dynamic components nanoparticles (Yang *et al*. 2009).

Nanoparticles Used in Biopesticides Controlled Release Formulations

The different types of nanomaterials used are,

1) **Nanospheres:** Active compound is dispersed into the polymeric matrix.
2) **Nanocapsules:** Active compound is lined by matrix polymer and centred in the core.
3) **Nanogels:** These are cross-linked polymers which are hydrophilic in nature and can absorb large amounts of water.
4) **Micelles:** These are aqueous collection formed by hydrophilic and hydrophobic molecules.

Classes of Nanoparticles

Based on morphology, structure, dimension and composition, nanoparticles are classified into five categories, carbon based nanoparticles, metal containing nanoparticles, quantum dots, zero valent metals and dendrimers. However, carbon based nanoparticles and metal containing nanoparticles are widely used.

i) Carbon based nanoparticles

Carbon based nanoparticles have unique structure as well as excellent mechanical, chemical, and optical properties. These are of two types, carbon nanotubes (CNTs) and fullerenes (Khan *et al*. 2017).

a) Carbon nanotubes (CNTs)

Carbon nanotubes are graphene sheets which are rolled into a tube, which provide structural support as they are almost 100 times stronger than steel. These nanoparticles are very unique as they are thermally conductive along the length and nonconductive across the tube.

b) Fullerenes

Fullerenes are carbon allotropes having sixty or more carbon atoms arranged in a pentagonal and hexagonal array in a hollow cage structure. These are commercially very useful because of their high strength and electrical and structural properties.

ii) Metal containing nanoparticles

Metal containing nanoparticles constitute the largest group of nanoparticles, which include oxides such as zinc oxide (ZnO), titanium dioxide (TiO_2), cerium dioxide (CeO_2), copper oxide (CuO), chromium dioxide (CrO_2), molybdenum trioxide (MoO_3), bismuth trioxide (Bi_2O_3) and lithium cobalt dioxide ($LiCoO_2$) (Buzea *et al*. 2007). These nanoparticles are extensively used in food, chemical and biological areas.

Biosynthesis of Nanoparticles

Nanoparticles can be synthesized by physical, biological or chemical method. The chemicals have adverse effects on humans and environment. The most economical, socially acceptable and ecologically reliable alternatives to chemical method is biological method. Green synthesis of nanoparticles is done by using enzymes (Willner *et al*. 2006), green plant materials (Shankar *et al*. 2004; Ahmad *et al*. 2011), microorganisms (Klaus *et al*. 1999; Konishi *et al*. 2007) and fungus (Vigneshwaran *et al*. 2007). The nanoparticles are synthesized with help of viruses, bacteria, fungi and plant extracts that are safe, cost effective, eco-friendly, biocompatible and green approach (Abdul *et al*. 2014). The chemicals are also used for the production of nanoparticles. There is a chemical bond present between active compounds and coating matrix such as polymer. The insecticide molecule can bind initially to the side chain of one monomer and then the polymerization reaction takes place or the polymerization occurs first and only after that, the biocide binds to the side chain (Wilkins, 2004). The nanoparticles were synthesized by using gold, copper, silver and other metallic oxides (Singh, 2012).

Synthesis of Nanoparticles by Using Bacteria

i) Silver nanoparticles

The extracellular and intracellular formation of Ag nanoparticles could be done by using various bacteria *Salmonells typlus*, *Pseudomonas aeruginosa, Pseudomonas stulzeri, Escherichia coli, Vibrio cholera* and *Staphylococcus currens* (Lengke *et al*. 2007). The metal ions were reduced to metals with the help of microbes. The photoautotrophic cyanobacterium *Plectonema boryanum* had been used for extracellular formation of silver nanoparticles (Lengke *et al*. 2007). The formation of silver nanoparticles in the range of 50 nm in size had been done with *Bacillus licheniformis* (Kalishwaralal *et al*. 2008). The treating of aqueous silver nitrate solution with culture supernatants of altered strains of Enterobacteria such as *Klebsiella pneumonia* was recently the most rapid method for the development of silver nanoparticles (Shahverdi *et al*. 2007; Mokhtari *et al*. 2009).

ii) Zinc oxide nanoparticles

Bacteria are used for formation of ZnO nanoparticles but selection of microbes for its synthesis is a laborious procedure. The whole process is to be required very keen observation and vigilant monitoring of culture broth. The *B. licheniformis* was very helpful for the synthesis of ZnO nanoflowers. These nanoflowers were in 40 nm in width and 400 nm in height (Raliya and Tarafdar, 2013).

Synthesis of Nanoparticles by Using Plant Extracts

i) Silver Nanoparticles

The technique for the green synthesis of Ag nanoparticles using the plant extracts is cost effective, ecologically reliable and economically sound. These extracts act as stabilization and reduction of silver ions (Kulkarni and Muddapur, 2014). The plant leaves were cleaned by using the tap water and distilled water in order to remove the dust and debris materials from the surface of plants. Then, 10 gram of leaves was taken and boiled in 100 ml of distilled water. The plant extracts were prepared. The $AgNO_3$ is to be added into the distilled water to make aqueous solution. The plant extracts were added drop wise into the aqueous solution of silver nitrate in order to reduce pure Ag (I) ions to Ag (0). This synthesized solution was monitored by the

UV-Visible spectrophotometer with the regular intervals (Krishnaraj *et al.* 2010).

ii) Zinc oxide (ZnO) nanoparticles

The ZnO is a semiconducting metal oxide that plays an important role in the field of optics, biomedical systems and electronics (Gunalan *et al.* 2012; Vanathi *et al.* 2014; Anbuvannan *et al.* 2015; Sundrarajan *et al.* 2015; Patil *et al.* 2016). It plays a vital role in the area of biomedical sciences by possessing antidiabetic, agricultural, antifungal, anti-cancer, drug delivery and antibacterial properties (Martiankova *et al.* 2009; Movahedi *et al.* 2014; Jain *et al.* 2014; Sangani *et al.* 2015; Hameed *et al.* 2016). The ZnO nanoparticles are safe, cost-effective and can be easily prepared (Jayaseelan *et al.* 2012). US FDA has enlisted ZnO as GRAS (generally recognized as safe) metal oxide (Pulit-prociak *et al.* 2016). The various parts of plants that contain toxic metabolites are used for nanoparticles synthesis. These plants are also acting as the stabilizing and reducing agent (Nagajyothi *et al.* 2013; Gnanajobitha *et al.* 2013; Zong *et al.* 2014; Nachiyar *et al.* 2015; Ramesh *et al.* 2015; Rajeshkumar, 2016; Xiao *et al.* 2016). The *Trifolium pratense* flower extract was used for the synthesis of ZnO nanoparticles and these were analyzed by UV-visible spectrophotometer in order to show various peaks and formation of stable nanoparticles. The *Rosa canina* and *Aloe vera* extracts was used as capping and reducing agent confirmed by the FTIR studies (Dobrucka and Długaszewska, 2016).

Synthesis of Nanoparticles Using Fungus

The extracellular formation of nanoparticles was done with fungus material (Azizi *et al.* 2014). The fungal strains have better tolerance and bioaccumulation property as compared to bacteria (Pati *et al.* 2014). The average size of nanoparticles was 3.8 nm synthesized by using fungus was examined by the atomic force microscopy (AFM) and dynamic light scattering (DLS) was used to check the average height of nanoparticles that was about 8.56 nm in size (Hoffmann *et al.* 1995; Pavani *et al.* 2012; Shamsuzzaman *et al.* 2013). The most widely used fungus species for the synthesis of nanoparticles is *Aspergillus* that has mostly spherical shape.

Synthesis of Nanoparticles Using Algae

Algae, a photosynthetic eukaryote and an oxygenic aquatic microorganism, have the property of bioaccumulation of heavy metals inward and outward. This character manifests algae as an inexhaustible raw source for the synthesis of nanoparticles (Castro *et al.* 2013). In the cell wall of various seaweeds, metal salt source gets reduced into nucleated nanoparticles

(Mahdavi *et al*. 2013; Kumar *et al*. 2013), whereas huge amphiphilic biomolecules direct and govern the nanoparticles growth (Stalin Dhas *et al*. 2012). Spirulina platensis, a blue-green algae, produced Au nanoparticles in which they have absorbed Au ions and manufactured Au nanoparticles intracellularly especially assembled in the vacuoles (Suganya *et al*. 2015). A marine brown alga *Ecklonia cava* was exploited to produce spherical- and triangular-shaped pure Au nanoparticles in the range of 30 ± 0.25 nm at 80°C within 1 minute. A recent study reported that green algae *Ulva armoricana* contain ulvan which is a sulfated polysaccharide and recognized as a stabilizing and reducing agent for the fabrication of Ag nanoparticles. Ulvan would be a promising alternative for citric acid as it's a natural stabilizer for Ag nanoparticles. Besides, it will serve as an advanced material to prepare antimicrobial compounds in the field of cosmetics and biomedicine (Massironi *et al*. 2019).

Synthesis of Nanoparticles Using Yeast

Yeast, a single-celled microorganism, possesses many advantages over bacteria due to their mass fabrication of nanoparticles. It is very easy to handle in laboratory circumstances and they synthesize various enzymes because of their rapid growth by consuming simple nutrients (Dameron *et al*. 1989). Yeast strain MKY_3 is used to synthesize Ag nanoparticles in the range of 2-5 nm extracellularly in high quantity without any loss (Kowshik *et al*. 2003).

Synthesis of Nanoparticles Using Biological Particles

Bioparticles like proteins, vitamins, virus, enzymes and peptides could act as a source to fabricate nanoparticles. Cowpea mosaic virus and cowpea chlorotic mottle virus have been exerted to mineralize the inorganic materials (Douglas and Young, 1998; Douglas *et al*. 2002). Crystalline and sulfide nanowires have been mineralized by tobacco mosaic virus (TMV) (Shenton *et al*. 1999). Peptides are efficient in nucleating the nanocrystal growth, whereas it was authenticated from the integrated screen and identified on the M_{13} bacteriophage surface (Mao *et al*. 2003).

Synthesis of Nanoparticles Using Biodegradable Waste

Our environment acts as a treasure of waste substances especially food wastes. However, it can be exploited for the different nanoparticles production, as its cell wall has various organic compounds like polysaccharides, dietary fibres, carotenoids, phenols, flavonoids, vitamins, and essential oils (Heim *et al*. 2002; Kim *et al*. 2012) which function as templates. Extract of mango peel has produced monodispersed Au nanoparticles in the range of 6.03 ± 2.77 to 18.01 ± 3.67 nm in size. Wine industries generated huge amount of grape waste which is actually a raw source of biologically organic molecules and reduced the metals into spherical shaped Ag nanoparticles with average size of 25 to 35 nm (Xu *et al.* 2015). The eggshell membrane of chicken is one of the nature's bonus, which is not edible and used for the fabrication of Au nanoparticles with fluorescence via one-step process under optimum conditions (Devi *et al.* 2012). It has amino acids which include alanine, glycine, and uronic acid and glycoproteins like collagen (Arias *et al.* 1991) which employed as a template for the production of Au nanoparticles (Devi *et al.* 2019). Custard apple *Annona squamosa* belongs to Annonaceae family which has anticancer, antimicrobial, medicinal and insecticidal properties (Dwivedi and Gopal, 2010; Madhumitha *et al.* 2012). It is edible and the peels were considered as waste; however, the peels consist of hydrophilic hydroxyl and ketone groups which actually account for the transition of silver ions into Ag nanoparticles and these groups offer stability by establishing thin layer on the surface of nanoparticles (Kumar *et al.* 2012).

Nanopesticides

Nanopesticides are biologically derived complexes with nanoparticles which are designed to be used as pesticides. Nanopesticides consist of organic ingredients such as polymers and inorganic ingredients such as metal oxides (Kookana *et al.* 2014). Nanoformulation has a significant role in the development of nanopesticides by increasing the apparent solubility of poorly soluble active ingredients and releasing the active ingredient in a targeted manner and protecting the active ingredient against premature degradation (Kah *et al.* 2013). There are many nanopesticides which are engineered with useful pesticidal properties and it has been shown to be effective against a variety of insects.

Salient Features of Nanoparticles Based Pesticide Formulation

1) Increased stability of formulation which prevents early degradation
2) More elimination of toxic substances compared to conventional pesticides
3) Improved mobility
4) Higher insecticidal activity due to smaller particle size
5) Larger surface area, which increases their longevity (Shah and Wani, 2016).

Benefits of Nanoparticles

Better and accurate delivery of products as they are designed to transfer particular molecules to a cell or tissue according to requirement. These nanoparticles enter into the plant cell by binding to some carrier protein or through ion channels (Singh and Lillard, 2009). Permeability of plant cell wall also plays an important role in this uptake. In spite of its advantageous effect on plants, these nanoparticles are being tested for its phytotoxicity. Different studies have reported different effects of these nanoparticles on seed germination and plant development. For example, it has been shown that ZnO nanoparticles promote seedling growth of mung and gram beans at a certain concentration whereas treating castor seeds with silver nanoparticles did not show any effect on seed germination nor on growth of lepidopteran insects on the seeds (Dhoke *et al*. 2011). Localization of nanoparticles in nucleolus or mitochondria, by scanning electron microscopy confirmed their penetration into cell organelles, which suggest their use for targeted delivery of pesticides.

Methods to Develop Nanoparticles for Pest Control

Pesticide encapsulation is essential for its controlled release as well as to minimize its toxic properties. There are many chemical and physical methods to develop nanoparticles loaded with pesticides. Some of the methods for developing nanoparticles with uses are described below:

i) Pesticide loaded nanoparticles

Some nanoparticles have the property of loading different kinds of pesticides such as insecticides, herbicides, fungicides and nematicides. Crooks *et al*. have made aqueous suspension of nanoparticles which contain an organic active ingredient such as pesticides. Many insecticides, herbicides, fungicides and miticides can be formulated with this technique. Pesticide-coated metal oxide nanoparticles, which is really helpful for controlling harmful insects, comprising a UV photo protective filter was developed by Ishaque *et al*.

ii) Insecticide loaded nanoparticles

Imidacloprid is a novel insecticide encapsulated with chitosan and sodium alginate and presents in a low amount in soybean plants (Guan *et al*. 2008). Deltamethrin, a silver nanoparticle conjugated to the pyrethroid pesticide was effective against arthropod vectors such as mosquitoes (Sooresh *et al*. 2011). Another nanoparticle, Pyrifluquinazon, which has a controlled release feature, was found to be effective against *Myzus persicae* (Kang *et al*. 2012). Polyethylene-glycol-coated nanoparticles were more effective against insect pests compared to essential oils (Yang *et al*. 2009). Nanogels loaded with cumin and ajwain essential oil showed more efficacy against insect pests compared to only oil-loaded nanogels.

iii) Fungicide loaded nanoparticles

Fungicide loaded nanoparticles were prepared using polyvinylpyridine (PVPy) and polyvinylpyridine-co-styrene and were loaded with Tebuconazole or Chlorothalonil fungicides as aqueous dispersions. This formulation was shown to be effective against many pathogenic fungi (Liu *et al*. 2003).

iv) Nematicide loaded nanoparticles

A nematicide loaded insecticide Lansiumamide B was prepared using the microemulsion polymerization method (Yin *et al*. 2012).

v) Herbicide loaded nanoparticles

Herbicide loaded nanoparticles have very low phytotoxicity on crops and are designed for slow and controlled release of active substances. Paraquat-loaded alginate/chitosan nanoparticles can change the release profile of a herbicide and its interaction with the soil (Silva *et al*. 2010). Eventually, herbicide loaded nanoparticles can be applied to reduce the negative impacts caused by herbicides. Glyphosate isopropylamine, a water soluble herbicide, was prepared using a green nanoemulsion system and it was shown to be effective against the weeds creeping foxglove, slender button weed and buffalo grass (Lim *et al*. 2013). Another nanoparticle loaded with Chloroacetanilide herbicide (Alachlor) was shown to reduce the degradation of the herbicide (Thompson *et al*. 2010).

Mechanisms of Action of Nanoparticles

Understanding the mechanisms is really important to predict the toxicological effects in using these nanoparticles as pesticides. The toxicity of silver nanoparticles is highly influenced by size, shape and charge of nanoparticles (Foldbjerg *et al*. 2015). One of the most accepted theories about the mechanism of action of nanoparticles is that they penetrate exoskeleton and bind to DNA and proteins, which lead to rapid denaturation of organelles and enzymes. Ultimately, disturbance in proton motive force and decrease in membrane permeability results in loss of cellular functions, leading to cell death. Some of the mechanism of action of nanoparticles and the pests to be controlled are summarized as below,

Sl. No.	Tested nanomaterials	Target insect/pest	Mode of action	References
1.	Nanodiamonds coated with Neb-colloostatin	*Tenebrio molitor*	Apoptosis of hemocytes and inhibited cellular and humoral immune responses	Wahab *et al*. (2015)
2.	Titanium dioxide nanoparticles (TDNPs)	*Helicoverpa armigera*	Reduction of detoxifying enzymes such as β-glucosidase and carboxylesterase and increase of glutathione S-transferase	Chinnaperumal *et al*. (2018)
3.	Ag nanoparticles prepared using extracts of *Cassia fistula*, *Euphorbia hirta*, *Mimosa pudica*	*Helicoverpa armigera*, *Aedes albopictus, Culex pipiens pallens*, *Rhipicephalus microplus*	Fourth instar larvae showed a decrease in total protein levels; nanoAg also reduced acetylcholinesterase and α- and ß-carboxylesterase activities	Marimuthu *et al*. (2011); Devi *et al*. (2014); Murugan *et al*. (2016); Fouad *et al*. (2018)
4.	Ag nanoparticles prepared using extracts of *Annona squamosa*	*C. quinquefasciatu*, *Anopheles stephensi*	Pupa and all larvae instars showed a decrease in total protein levels; nanoAg also reduced acetylcholinesterase and α- and ß-carboxylesterase activities	Arjunan *et al*. (2012)
5.	Ag nanoparticles prepared using extracts of root of *Delphinium denudatum*	*A. aegypti*	Second-instar larvae showed a decrease in total protein levels	Suresh *et al*. (2014)
6.	Ag nanoparticles prepared using leaf aqueous extract of *Aloe vera*	*A. stephensi*	All larvae instars showed a decrease in total protein levels	Dinesh *et al*. (2015)
7.	Ag nanoparticles prepared using leaf aqueous extract of *Phyllanthus niruri*	*A. aegypti*	Larvae showed a decrease in total protein levels	Suresh *et al*. (2015)

8.	Ag nanoparticles prepared using extracts of *Mimusops elengi*	*A. stephensi* and *A. albopictus*	--	Subramaniam *et al*. (2015)
9.	Ag nanoparticles prepared using extracts of leaf aqueous extract of *Manilkara zapota*	*Musca domestica*	Adult stage showed a decrease in total protein levels	Kamaraj *et al*. 2012
10.	Ag nanoparticles prepared using leaf aqueous extract of *Tinospora cordifolia*	*Pediculus humanus capitis*	--	Jayaseelan *et al*. (2011)
11.	Ag nanoparticles prepared using using leaf extracts of *Feronia elephantum*, *Heliotropium indicum*	adults of *A. stephensi*, *A. aegypti*, and *C. quinquefasciatus*	--	Veerakumar and Govindarajan (2014)
12.	Ag nanoparticles prepared using *Phyllanthus niruri*	*A. aegypti*	Suppressed adult female fecundity, egg hatchability, and reduced longevity in both sexes	Suresh *et al*. (2015); Madhiyazhagan *et al*. (2015); Roni *et al*. (2015)
13.	Ag nanoparticles prepared using some fungi such as *Chrysosporium tropicum*, *Trichoderma harzianum*, *Fusarium oxysporum*, *Cochliobolus lunatus*	Mosquito species	--	Salunkhe *et al*. (2011); Soni and Prakash (2012, 2013); Sundaravadivelan and Padmanabhan (2014)
14.	Ag nanoparticles fabricated using salicylic acid and 3,5-	*Aedes albopictus*, *Spodoptera litura*, *Achaea janata*, *Lygus*	4th instar larvae showed a decrease in total proteins, esterase, acetylcholine	Debnath *et al*. (2012); Yasur and Rani (2015); Gaal *et al*.

	dinitrosalicylic acid	*hesperus* and *Acheta domesticus*	esterase, and phosphatase enzymes	(2018)
15.	Ag nanoparticles	*Drosophila melanogaster*	Accumulation of reactive oxygen species (ROS) leading to ROS-mediated apoptosis, DNA damage, and autophagy; activation of the Nrf_2 dependent antioxidant pathway	Mao *et al*. (2018)
16.	Nanostructured Al_2O_3	*Sitophilus oryzae*	Bind to the beetle cuticle due to triboelectric, results in insect dehydration forces, sorbing its wax layer by surface area phenomena, resulting in insect dehydration	Stadler *et al*. (2017)
17.	Au nanoparticles fabricated using latex of *Jatropha curcas*	*Aedes aegypti*, *Spodoptera litura*, beetles, mealy bugs	Triggered trypsin inhibition	Chakravarthy *et al*. (2012); Chandrashekharaiah *et al*. (2015); Patil *et al*. (2016)
18.	Graphene oxide nanoparticles	*Acheta domesticus*	Increase in enzymatic activity of catalase and glutathione peroxidases, as well as heat shock protein (HSP_{70}) and increase in total antioxidant capacity levels	Dziewiecka *et al*. (2016)
19.	TiO_2 nanoparticles	*Bombyx mori*	Upregulation of PI3K and $P_{70}S_6K$ [mTOR pathways]; 4 cytochrome P_{450} genes were upregulated; 20-hydroxyecdysone biosynthesis was stimulated; reduced	Li *et al*. (2014)

			development and molting duration were noted	
20	Ag nanoparticles	*Drosophila melanogaster*	Loss of melanin cuticular pigments, reduced activity of Cu-dependent enzymes (tyrosinase and Cu-Zn superoxide dismutase)	Armstrong *et al*. (2013)
21.	SiO_2 nanoparticles	*Bombus terrestris*	Leads to midgut epithelial injury in intoxicated workers	Mommaerts *et al*. (2012)
22	Ag and TiO_2 nanoparticles	*Drosophila melanogaster*	Loss of progeny and a decrease in developmental success	Philbrook *et al*. (2011)
23.	Polystyrene nanoparticles	Insect cells (BACULOSOMES®)	Inhibited the enzymatic activity of CYP_{450} isoenzymes in BACULOSOMES®	Frohlich *et al*. (2010)
24.	Carbon black and multiwalled nanotubes	*Drosophila melanogaster*	Nanomaterials adhere strongly to fly body parts which leads to impaired motor functions, resulting in insect mortality	Liu *et al*. (2009)
25.	SiO_2 nanoparticles	Different species, with special reference to stored product pests	Physio-sorbed by the insect cuticular lipids, causing major damages, followed by insect death	Barik *et al*. (2008), Debnath *et al*. (2011) and Athanassiou *et al*. (2018)

Conclusion

Chemical pesticides are very effective but associated with deleterious effects on other animals as well as human beings. Moreover, due to the continuous use of chemical pesticides, useful soil microbes as well as natural enemies are destroyed that lead to pest resistance. However, traditional strategies are insufficient for the control of pests in very large areas. Nanotechnology, a relatively recent field, can be an alternative approach for the management of insect pests in agriculture without negatively affecting nature. Furthermore, combining pesticides with nanoparticles will have more specific and targeted effects on pest populations. This will also reduce the burden of pesticides as combining even a small amount with nanoparticles will have a significantly stronger effect. Though there are some toxic effects of nanoparticles on some aquatic organisms but not on beneficial insects. This gives an opportunity for further research and validation with the aim of completely harnessing the potential of nanoparticles and nanotechnology in the agricultural field.

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Chapter - 8

Consequences, Problems & Preventive Solutions of Drug Addiction

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Chapter - 8

Consequences, Problems & Preventive Solutions of Drug Addiction

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Abstract

Drug Addiction is spreading in the society like a fire in the forest. Not only youngsters, not only females rather kids are also indulged into this menace. Female drug addiction may lead to the birth of physically and mentally challenged infants. Addiction in kids and youngsters may spoil their happy & prosperous lives, not only their own rather of their families too. It's need of the hour to curb the menace as soon as possible. Anti - Narcotic Department & Governments should take severe actions to stop this malpractice. It's over the throat now, we should aware our kids and youngsters against the drugs and other intoxication, otherwise it will be too late to control. We all have been blessed with a single beautiful & purposeful life, if that will be spoiled then there will be no second chance for the same. Drugs are meant for treatment, cure & prevention of diseases let them be for the same causes only let's not take drugs for intoxication and deterioration of the health. Healthy mind dwells in healthy body, if we deteriorate our health our mental health will also get adversely affected. Not only the doer rather his family, his near & dears also get badly affected. Let's get indulged into sports, cultural activities, education and spirituality to get rid of this drug addiction. Do not keep yourself idle, as idle mind is devil's workshop. Keep yourself busy in productive tasks so that we do not get free time to think of deteriorating things like drugs, robbery, thieve, mischievousness and other illegal things. It should be our collective responsibility to curb the menace by working shoulder to shoulder with the Governments and other agencies. Proper action by administrations on the druggies & drug peddlers, their social & spiritual awakening is the only solution to curb this root cause of the disease of drug addiction.

Keywords: Drug addiction, druggies, drug peddlers, anti-narcotic, spiritual awakening.

1. Introduction

We all are always in search of happiness and contentment in our life. Our own happiness is not related to ourselves only rather all our family members and near & dears are also connected to it. In this materialistic world we have three types of happiness; physical, mental and monetary i.e. related to body, brain and wealth. By physical happiness we mean a state of good health, good lifestyle i.e. a body free from diseases and ailments, by mental happiness we mean peace of mind, satisfied and contented life, by monetary happiness we mean good sources of income, we should not have any scarcity of any materialistic things in our life. All these happiness are gone when we get addicted to drugs and other intoxications. Whether social, spiritual or personal life is concerned, all these get vanished. Not only a doer rather his family his surroundings and ultimately the whole society gets adversely affected. As we all are living in a family and society, so, bad influence on the family as well as society is expected. We all have only one life, if that one golden chance is wasted there will be no retake for the same. We are living in a real life, not in the reel life where we can get the second or third chance, so, we should take care of this golden chance very precisely. A person in his life has the potential to refurbish his entire life, not only his own but for his family and other near and dears, if that time is wasted in taking drugs etc then there will be total loss which can never be reimbursed. Initially one may enjoy or feel pleasure in doing so but later and ultimately he or she has to repent for the same. In the initial phase our body can bear these severe jerks due to drugs and intoxications but later on all our body organs cannot bear these and hence ailments and sufferings get started. In the year 2019 the deaths due to drugs and alcohol consumption was over 5.6%, in the year 2020 the proportion was increased to 6.0% and it is increasing day by day. In India suicide cases due to drug addiction and other intoxications were maximum in Maharashtra and Karnataka. It’s a very serious issue, now it’s over the throat, we must think of it that how to eradicate it properly from our society, otherwise it will be too late. Let’s indulge our youth in sports, cultural activities and other co–curricular activities so that they cannot even think of this drug abuse. We all know that idle mind is devils workshop, so, let’s keep ourselves busy in sports, education, entertainment and by all other means so that we don’t have free time to get indulged into bad and useless habits. Competitive spirit in youth should be there in every positive way, so that they can compete even with their own and become more and more refined in every step. In our songs, albums, movies and other social sites such issues should be raised, so that every single youngster should be aware of such menaces. Media has great and very significant role in reforming as well as deteriorating the youth. In media and film industry thoughtful and insightful movies and documentaries are formed so that we get used to them, we should be familiar with that scenario. Actually we always try to do what we see in our surroundings. If we have neat and clean environment and scenario we will always be neat and clean in our behaviour. There will be no ill will, no mismanagement and no addiction to drugs etc. Spiritual awareness is also needed as a preventive measure, as in our scriptures there are commandments to beware of drugs, intoxications and other narcotics. A spiritual awakened person is always very insightful, thoughtful and good decision maker. Spiritual awakening always tell us to do introspection, and by introspection we get to know self realization. Once we have self realization, we would know what to do and what not to do. It is said that the first sign of being eligible is that you have known where you are ineligible. Even it is said that self realization through God's Realization i.e. if you have self realization then you must have God's realization too and vice versa. So, Spiritual connectivity or being adhere to spiritualism is a big factor to get away from such drugs and intoxications. During the present times we are unaware of this spiritual aspect to eradicate drug addiction from our society but if we will take care of it, it will be very helpful to curb the menace. Spiritualism always inculcates good habits and good etiquettes along with patience and tolerance in the humans. So, spiritual awakening in the youngsters will bring a paradigm change in them. Right from the schools to college level and then to the universities there must be regular awareness campaigns, so that we can brainwash of all the youngsters. Mostly from the age of 12 onwards kids are prone to behaviour change due to hormonal change in their bodies, if they are not properly taken care of, they might go into wrong direction and get deviated from their actual paths. As prevention is always better than cure, so, preventive measures are to be taken so honestly and sincerely that we do not require any rehabilitation centers in future again. That day will be the golden day when there will be no youngster in the rehabilitation centre rather all will be enjoying their lives to the fullest in achieving laurels in the field of education, sports, cultural activities and other co-curricular activities. There would be dancing & singing youngsters with smile and shine on their faces. Free from drugs and intoxications enjoying healthy & wealthy life.

2. Consequences & Problems Caused Due to Drug Addiction

1) Physical, Mental and Monetary Loss

We have three types of pleasures/assets in our life i.e. good physical health, peace of mind and wealth for household & other various tasks of life. If we get drug addicted then all of these three assets get lost. Moreover, not only of the doer rather all his/her family members and other near & dears get badly affected. One drug addicted person may adversely affect as an average of 15 persons directly or indirectly. His habits may have long lasting effects on his family, particularly on his children. These days as per news papers and news channels if we see many females are being drug addicted. It is utmost dangerous and alarming issue. If a female is drug addicted, her newly born kids or even before their birth, their health whether physical or mental could be badly affected, which will go through out their life. A smoking mother may give birth to a child with cancer prone diseases or other infections. If we want to save our present generation and coming generations then it's the need of the hour that we must curb this menace of drug abuse as early as possible.

2) Social Cut Off

Drug addicted person keep on thinking of his own; about the drugs and intoxication only because otherwise he is incapable of doing any task. Moreover, after taking drugs and some other options of intoxication he attains a different state of mind, which makes him away from social involvement to a solitary life. He doesn’t need any companion or friend to talk and spend time with, he becomes dependent on the drugs only otherwise his body will not allow him to do any work. In social life a person should be active enough to solve his own as well as other's problems but addicted persons become lethargic, incapable and inefficient to take any decision. So, his social circle becomes only with his own type of people and ultimately he gets aloof from society and gets lost in his own dome of darkness.

3) Poor Decision Making and Loss of Self Confidence

It's not in very early stage but with the passage of time a drug addicted person gets detached from all his responsibilities and duties because he becomes now an incapable person. He cannot think without his drugs and other intoxication he is addicted to. His thinking capacity becomes limited to his own demands only. He has shattered confidence and poor decision making. Confidence can be build when a person becomes skilled in his own field but an addicted person has no field except his drugs and other intoxication. Moreover, nobody asks him for opinion and important decisions and ultimately he becomes away from this sphere of life. Neither an addicted person takes his own decisions nor others want to take opinion from him because they all know that now he is not in that state of mind. So, ultimately drug addiction leads to poor decision making and loss of self confidence in him.

4) Wastage of Precious Time

It is rightly been said that stitch in time saves nine i.e. who are time bound and punctual in their life they are free from hustle and bustle of life. In our life time is very much important. If we will waste time, in turn time will waste us. If we are unable to do a particular task at a particular time or in prescribed time then it may come out to be useless. We all have one life; if that life is wasted in drugs etc. then we will not get any chance to repeat it again. So, our time is very much precious we should not waste it in useless and futile tasks. Wisdom lies in the fact that we should utilize our routine life in significant and fruitful tasks. Our efforts should be beneficial for us, for our family and for our society. Time always drifts on but memories stay. By precise usage of time we should decorate our life rather than wasting it in one or another ways. The life of a drug addicted person is a total waste. It must be clear in our mind that due to these drugs and other intoxications we are not just wasting our own precious time of life rather we are wasting the precious time of all related to us. We can even make a stoppage to the success and happiness of our coming generation by doing so. Nevertheless, we should not lose hopes and just think every new day is an opportunity given by God to rectify our mistakes and to do new fruitful tasks. We all should have an optimistic approach in our life. In this way all of us and hence our country will grow precisely.

5) Addiction in Routine Life

In the initial stage it may give pleasures and more active state but when addiction comes to routine life then its adverse effects start coming and spoiling our life. Starting from the morning till the sleeping time his efficiency becomes almost 40% of his actual. Its normally said that excess of everything is bad means even the excess of good things become bad but if the excess of bad habits is there then one can better imagine what will be the future of that person. Regular smoking habits damage your lungs, liver and respiratory system. Immune system will reduce and chronic diseases like cancer etc. become more probable. In our routine life we have to spend time with parents, children, and other family members along with some other social tasks besides our professional work load. However, if we got addicted to such intoxications etc. then we will not get quality time to spend with, so, ultimately our life becomes zero or useless with time. Finally, I can say that a routine drug addicted person is good for nothing.

6) Invitation to Many Diseases Leading to Death

It must be very clear to everyone that taking drugs and having intoxications is not just a bad habit rather it leads to invite many dreaded diseases like liver infection, lungs infections, heart problem, kidney spoilage, cancer etc. and many more which becomes chronic and may lead to even death. In India there are more than 10 deaths everyday due to this Drug addiction. It is aptly said that prevention is always better than cure. So, we should not go on the track of diseases by taking intoxications rather we should avoid that path just by avoiding them in our life. Health lost is equal to loss of pleasures and happiness in the life. If we have to see importance of good health just visit a hospital and have a look on the heart patients, kidney patients or cancer patients etc. and ask them what is there experience of life, what are the restrictions imposed on their eating, drinking and other routine life style. We will definitely understand the significance of good health. Health is wealth and it is a hundred percent true and practical quotation. Healthy brain dwells in the healthy body. So, avoid drugs and other intoxications and lead a healthy, happy and cheerful life and let your near and dear ones to do the same. Final message is “Live and let live”.

7) Spiritual Break Down

It is written in our scriptures that drugs and intoxications are harmful for our body and brain. Such things take us away from God and our religion. The fact is that when we are used to intoxications etc. then our thinking gets changed which attracts us towards the monetary and materialistic things and we get separated from our religion and divine commandments. After taking intoxications we are senseless and get deviated from our actual path we are born for. For a religious person his spiritual, social and professional aspects are properly balanced, however, drugs and intoxications create imbalance among these three. According to commandments in our scriptures we should avoid such life spoiling intoxications to get attached to God as well as to lead a salvation of life. In nutshell I can say that avoid intoxications and drugs as these are prohibited for us as per the divine orders and it is our duty to obey them for blissful life. Otherwise, we will get spiritually separated.

8) Single Track Approach in Life

In our life we have different aspects, different tasks to do, many problems to solve, many things to celebrate and a lot of things to share & discuss. However, if we are drug addicted person, we have only one aim and that is to fetch drugs and consume them, nothing else. Our approach becomes just of single track; we think of intoxication, we live for intoxications. Other things of life like our family, our friends, our household tasks, our duties and other spiritual & social responsibilities appear insignificant for us. Hence, we lead a self centered and selfish life, which is not useful for us as well as for others. Ultimately our life becomes a burden for ourselves, good for thing and useless. To avoid such situation we should avoid drugs.

9) Bad Social Circle

Drug users are comfortable in the company of other drug addicted persons. They have only one type of approach, they don't think of social and personal aspects of life rather they are neck deep indulged into intoxication only. Along with taking drugs and intoxication they are prone to other anti social and illegal activities and ultimately they become burden on the society. Man is known by the company which he keeps. A drug addicted person always have such bad companies, rather he himself is an active member of that company and may be responsible to spoil others too. Generally, we say that our child is good but his bad company spoils him and do not ever think that he is the member of that company he might be responsible to spoil others. So, its wisdom to stop giving lame excuses rather let’s try to rectify the actual problem, which is the root cause of the disease.

10) Females Drug Addiction and Its Very Adverse Effects

These days from the society the different news are coming to us that many females are indulged into drug addiction and other intoxication. Such cases are increasing day by day, which is an alarming signal for our society. Females are the strongest pillar of our society especially of our family. If females get indulged into this addiction, who will take care of our kids and coming generations because these are the females who affect more to the children at home. Moreover, females have the divine character to give birth to a child, so, if a female is drug addicted, her child will be unhealthy and prone to many diseases like miscarriage, preterm birth, birth defect like damaged or abnormal development of fetus, SIDS (Sudden Infant Death Syndrome) etc. A Drug addicted mother can make her own life at risk as well as the life which is yet to begin for her child. Female drug addiction is more harmful and dangerous for our family and society. A male druggie can spoil himself, his family and society but a female druggie can spoil the coming generations too. Initially females also find pleasure and happiness in taking drinks, having flavored tobacco hookah and other intoxicated options but soon they will get addicted to it and it becomes difficult for them to get rid of all these. Now they are incapable of inculcating good moral values into their children because they themselves are deviated from their actual and precise life style. Some people just say that taking alcohol and tobacco just like medicine is good, however, I would say that take actual medicine rather but not these intoxicated alternative just by supposing that they will not be harmful. Our life is very much precious; don't let it get wasted, as we don't get another chance to retake. All these drugs and intoxications are very much harmful; kindly avoid them for our better tomorrow.

3. Preventions, Precautions and Solutions

1) Interest in Sports, Cultural and Other Co-Curricular Activities

Youngsters should take interest in sports, cultural and co-curricular activities to keep busy in such beneficial tasks rather to sit idly and get indulged into drugs and intoxications. In our mind generally bad ideas come, as it is said that idle mind is devil's workshop, so, keep this mind busy in sports and other fruitful activities. Watching sports is not just killing the time rather it is using the time for the betterment and happiness in life. Sports encourage us to live life lively and enthusiastically. Sports inculcate competitive spirit in youngsters; desire to be fit and fine, looking smart and handsome etc. Doing sports is a very good habit it takes us away from many diseases too. If kids are taking interest in doing sports from their childhood then their growth and health is far better than who do not do the same. If we are taking part in sports and all that, then it's far better but even if we are watching sports and enjoying, then it is also a good habit; at least we are not sitting idly or doing useless tasks which are harmful for our health.

2) Habits of Gymming, Doing Exercises & Yoga

To get up early in the morning before sun rise is an excellent habit. Moreover, if we are getting up early morning and going for a morning walk and taking fresh oxygen in the cool environment then it's excellent, however, if not in the morning then in the evening we can do the same. At least once in a day we should spare time for our physical maintenance. Going to gym for exercise either in the morning or evening is also a good for health. Sometimes, going to gym or going for a morning or evening walk is not possible then we can do yoga too. For good physical and mental health yoga and exercise are a good option. Otherwise when we fell ill then we get alert for the same, however, it's better to think of it on the priority basis. If we are having such fruitful habits then we will not be into possession of drugs and intoxications at all. Good health maintains good thinking too, so our thinking will be positive and we would have positive approach in our life. We must spare our routine time in yoga, exercise, walk or gym to have a healthy life and healthy approach. Once we have such habits in routine we will not get attracted towards taking drugs etc. Nevertheless, many youngsters use steroids and other drugs during gym also which is obviously a bad habit, it should be nipped in the bud. Avoid drugs & intoxications and maintain your good physical and mental status by yoga, exercise and taking balanced and good diet.

3) Awareness for Drug Abuse

Most of us are aware of the menace of drug abuse and its consequences; still it's the need of the hour that there should be awareness campaign regarding this issue, so that everyone should be clear about it, its bad results and its deadly aspect. Sometimes, we don't think much of the consequences and get indulged into drugs and other intoxications; in those cases awareness camps are helpful. It's our duty to aware the youngsters to not to take drugs etc. Many educated and children from good family background are indulged into this menace, may be freedom of their parents or unawareness/ignorance at their own level is responsible for this cause. Many youngsters don't know the adverse effects of drugs on their body and mental health, they don't know even chronic diseases may start or even death may occur owing to same. Awareness is quite helpful in controlling the menace, so, regular and proper awareness should be provided either through camps, social media, in school, college and university levels etc.

4) Spiritual Awakening

We all have spirits in our bodies, so, we are connected to spirituality, directly or indirectly. Our scriptures are our literature; if we read them, then we will get aware that there are commandments written in them that we should avoid drugs, alcohol and other intoxications. So if we are connected to our religion or spirituality firmly then we will get rid of all these bad habits. Spirituality makes us calm, contented and satisfied in life. We should also spare time for or scriptures and spiritual awakenings given for us. We have lots of spiritual literature in books and in digital forms; we must watch that to, so that we can learn how to lead a peaceful and successful life. In our scriptures many dos and don'ts are given for us. Hence, if we are connected to spirituality we will be away from all the bad deeds including this drug abuse.

5) Membership of Youth Clubs

Youth clubs should be created for the betterment of the youngsters, where they can get together for sports, cultural activities, co-curricular activities, social issues, singing & dancing, painting, swimming, playing & watching games etc; so that they don't get time for negative thoughts, drugs and all that. Youngsters should have competitive spirit in games, scoring good marks, having physical fitness, having higher qualification etc. When we are members of such clubs of good people then automatically good habits start inculcating in us and we get rid of all the bad deeds. Let’s create and join such groups/clubs for our good thinking and hence a better tomorrow because what we think today will make our tomorrow accordingly.

6) Habit of Spending Quality Time with Family

We all know that up to 10 or 12 years of age kids are under the shelter of parents and family, till then they are free from bad habits of drinking and intoxications etc. Once they start living independently with friends they start having bad habits. It’s the duty of the parents and other family members that they keep eyes on their children and their friend circle too. Our kids are our future; they should be properly taken care of. What are their demands, what are their likings and priorities; we should know all these. We should develop such a scenario with them that they feel comfortable with families. Once they have habit of spending time with family they will not deviate from their paths. Family is a platform where only love prevails. All have true love for each others. So, spending time with family members will solve all the issues properly and precisely.

7) Governments Should Be Strict in Action

We all have our duties and rights, however, generally we think of our rights to the maximum and duties to the minimum. When we get fail to do our duties then it’s the responsibility of the Government to take action so that all the duties should be obeyed by all the residents. When awareness camps, social restrictions, regular requests are not enough to curb the menace then Government should take strict actions too. Strict actions should be taken on the druggies and very strict actions on those who are running drug rackets and doing drug peddling etc. It’s very important to abolish drug rackets; they are not just selling drugs rather they are involved in all other bad deeds like human trafficking, murders, kidnapping etc. Once youngsters get involved in such rackets they are also forced to perform all such activities too. So, it’s the need of the hour that Government should take severe steps to curb this menace either through strict actions on drug rackets/peddlers or proper functioning of rehabilitation centers where the druggies can get rid of the same.

8) Proper Guidance & Check in Schools, Colleges & Universities

Our schools, colleges and universities are the temple of learning. It’s our duty to spread such learning from these institutions amongst the students that what are dos and don’ts in our life. What should be our duties and what should we avoid in life. In a survey covering 6000 schools in Delhi, it was found that over 10% students from class 8-10 were indulged in drug abuse, which is very alarming. Fortunately or unfortunately we are very advanced now, we have very advanced technology, we are trying to walk on the moon but unable to walk properly on the earth. Likewise, in our schools, colleges and universities we are being taught about technologies, computers, mars, global warming and ozone layer etc. but we are unaware of what our kids are doing, where are they going. We are giving them degrees, not making them educated. Moreover, if education is being given, that is related to their qualifications only not for their day to day life. Let's make our students a better human being also; let's teach them the lesson of humanity also. Lectures on moral values, humanity, dos & don'ts, should also be there periodically. Moreover, a proper check on the student's activities in the campus and hostel should be there and proper actions should be taken regarding the same; proper disciplined atmosphere should be created. It's also need of the hour to curb the menace.

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Chapter - 9

The Role of SnO_2 Semiconductor Photocatalyst in the Photocatalysis

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Chapter - 9

The Role of SnO_2 Semiconductor Photocatalyst in the Photocatalysis

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Abstract

Contaminated wastewater treatment has become one of the most important problems in the world. Several remedial solutions to treat the wastewater from industries and domestic use have been developed. Semiconductor photocatalysis have been used to treat this toxic wastewater due to its several advantages. SnO_2 is widely used by several researchers for the demineralization of contaminated wastewater due to its low bandgap and low e/h pair recombination rate. The future research and knowledge gap need to be discussed to face the challenge of semiconductor photocatalysis.

Keywords: Photocatalyst, environmental remediation, activated carbon, nanoparticle

1.1 Introduction

As the global population and economic development is continuously increasing, contaminated wastewater problem have emerged as a global issue over the last decade [1-2]. Toxic organic compounds released from domestic wastes and local industries are the main polluting sources. In this context, it is necessary to find new technology for the wastewater treatment. The increase in global awareness regarding the environmental contamination stimulates the researchers to find the solution to solve this issue. Among various approaches to find remedy the biological treatment, chemical treatment, nanofiltration, electrodialysis, reverse osmosis etc. are already been proposed [3-5]. The major disadvantage of all these techniques is that these are costly, unable to do complete cleaning and many converts one phase of pollutant into another phase only.

Semiconductor photocatalysis is found to be a promising solution and extensive research has been carried out in last few decades. Fujishima and Honda [6] introduced the word photocatalysis and worked in this field of green technology using TiO_2 photocatalyst. Semiconductor photocatalyst under the irradiation of photons results in the photocatalysis which is a catalytic process [7]. This is an important technology commonly used for the photocatalytic wastewater purification, H_2 gas production from water splitting and solar cells. However, the wide range of applications of photocatalysts is restricted by high rate of recombination and less separation of photogenerated e/h pair. Therefore the synthesis of efficient photocatalyst with less e/h pair recombination is major challenge in front researchers. The efficient photocatalyst can provide an industrial application for the wastewater demineralization and H_2 gas production.

Sun is the prominent source of energy having wavelength 100 nm to about 1 mm (1,000,000 nm). About 95% of the solar light is get absorbed by the various atmospheric layers before reaching to the earth. Only 5% of the radiations reach to the surface of the earth. Near about 40% of the total radiations which reach to the surface of earth composed of visible light (Figure 1). These visible range radiations are capable to carry out all the photochemical reactions on the earth.

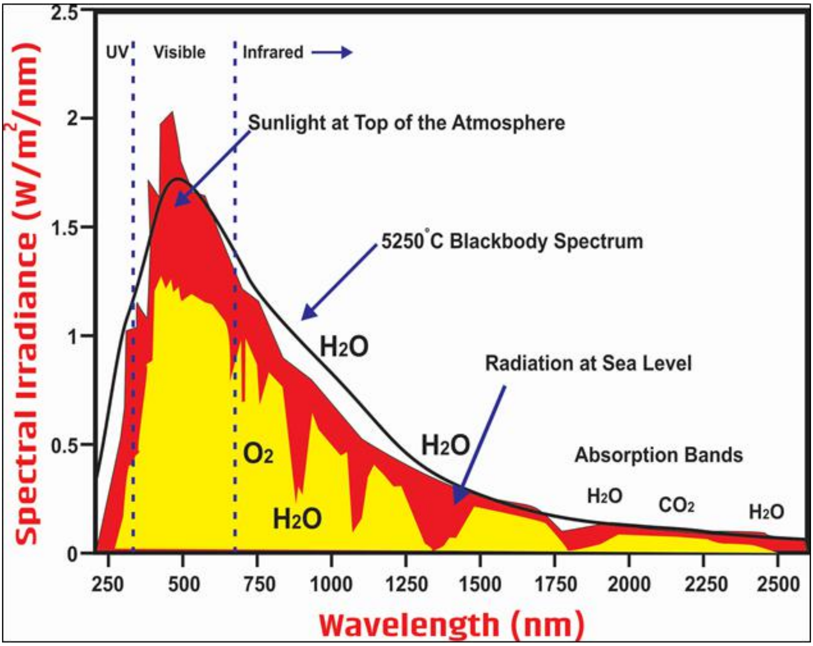

Fig 1: Solar spectrum

The researchers in the field of photocatalytic technology are promoted towards the maximum use of solar light for wastewater treatment and other applications.

1.1.1 Semiconductor photocatalysts

Semiconductor photocatalysis is an important industrial and green method to solve various environmental water pollution and energy problems using solar energy [8]. This is an environment friendly technology as the pollutants decompose into CO_2, H_2O and mineral acids [9]. The semiconductors work as a photocatalyst due to its electrical configuration. Band theory explains the two bands i.e. valence band (VB) and conduction band (CB) are the important concepts in semiconductor photocatalysis. Narrow band gap (< 3eV) is the significant intrinsic property of semiconductor. This leads to easily excite electrons from VB to CB. For every excitation of electron it leaves positive hole in the VB. The bandgap of various semiconductors is mentioned in Table 1. However the photocatalytic efficiency of these photocatalysts is low due to high e/h pair recombination. Accordingly, they are observed as not suitable for their industrial applications. In the present era, researchers focus on to enhance its photocatalytic performance and applications.

Table 1: The bandgap of various semiconductors

Sr. No	Semiconductor photocatalyst	Bandgap (eV)
1	TiO_2	3.2
2	WO_3	2.6
3	SnO_2	3.8
4	ZnO	3.2
5	CdS	2.25
6	GaAs	1.4
7	GaP	2.25
8	CdSe	1.7
9	Fe_2O_3	2.1
10	SiC	3.0

1.1.2 Role of supporting materials in the photocatalysis

Semiconductor photocatalyst supported on various materials which having large surface area such as alumina, zeolites, mesoporus materials or carbon based materials is a subject of research in past few decades [10-11]. The commonly used porus supporting materials generally have high surface area i.e. > 100 m^2gm^{-1}. The original principal principle behind the used supporting material for semiconductor photocatalysis is to decrease the dispersion as well as coagulation of photocatalyst and to increase its effective surface area.

The factors affecting the photocatalytic efficiency of supported photocatalysts are

i) Support pretreatment
ii) Method of preparation
iii) Nature of supporting materials
iv) Active species
v) Calcination

The possible applications of supported photocatalyst are depend on the support to develop robust catalyst. The support materials used in supported photocatalyst must be chemically stable, porus, having high surface area, mechanical integrity etc. The high surface area of the supporting material increases the active sites of the photocatalyst as well as it maintains the dispersion and coagulation of the powder photocatalyst [12]. This results in the enhancement of the photocatalytic activity of the supported photocatalyst. The type of supporting material used for the photocatalysis is critical factor for its commercial application. Amongst various supporting materials, the carbon based materials are of tremendous interest due to their porus structure, high surface area, high adsorption capacity and electronic property [13].

The advantages of carbon based materials are

i) Inert in several chemical reactions.
ii) Large number of active sites available for catalysis.
iii) High dispersion of the catalyst on support.

1.2 Water treatment

For the improvement in the living standard of human various chemical compounds have been invented and produced in industries. Near about 0.7 million tons of dyes are produced in various industries like textile, paint, cosmetics, leather etc. [14-15]. During dye production approximately 20% dyes have been lost and released into wastewater. As these dyes have carcinogenic properties so its high concentration in water is a major concern. Additionally, these dyes in wastewater undergo various reactions like hydrolysis, anaerobic discoloration or oxidation to produce several carcinogens this may prove hazardous to aquatic and human life. Thus, it is necessary to remove these pollutants from wastewater before discharging them into the environment. However, the scarcity of proper disposal procedure of these toxic chemicals often results hazardous for the human health. Wastewater treatment and availability of clean drinking water these are one of the important challenges in 21st century. The growing industrialization and growth in population has created a great concern about treatment of wastewater from industry and domestic use. Many toxic contaminants from industrial wastewater get mixed with underground fresh water and hence create threats to aquatic and human life [16]. Near about 90% wastewater from industries is discharged usually into lakes, rivers and costal zones [17]. As shown in Table 2 there are various methods commonly used to treat this wastewater Moreover, due to existence of metal ions and recalcitrant compounds in it have worsened the situation and compromises the quality of drinking water. In order to solve this problem and to increase the availability of clean drinking water new, eco-friendly and cost-effective method for wastewater treatment is needed.

Table 2: Different methods used for water treatment

Sr. No.	Methods	Description
1.	Adsorption	In this method the atoms or molecules show adhesion on the solid surface. During adsorption the phase of contaminants show change without degradation. The adsorption is depends on the surface area and adsorption capacity of the solid support.
2.	Chemical Oxidation	Use of certain oxidizing agents shows alteration in molecular structure of contaminants. This process may show formation of carcinogenic as well as mutagenic substances which are hazardous to human health.
3.	Biological treatments	The degradation of organic compounds can be achieved through living systems like algae and bacteria. This method is cheap and safe compared to other methods. The production of huge sludge is the only drawback of this method.
4.	Membranes	This water treatment method is based on the size of physical barrier. High pressure is generally used for this method as a driving force.

1.2.1 Photocatalyst and criterion for photocatalysis

The catalyst is the material which increases the rate of reaction without changing the Gibbs energy of reaction [18]. Generally, the catalytic reaction takes place at low temperature, normal pressure etc. There are two types of catalysis: Homogenous and Heterogeneous. When reactants and catalyst are present in similar phase then the reaction is homogenous catalysis. However, when the reactant and catalyst are not in similar phase then the reaction is known as heterogeneous catalysis. There is an interface between both catalyst and reactants in heterogeneous photocatalysis. The word photocatalysis was introduced in 1930 and then the definition ‘a catalytic reaction involving light absorption by a catalyst’ was recommended by IUPAC. Subsequently, the photocatalysis become very famous because it shows easy and complete demineralization of organic pollutants without production of any hazardous waste.

The position of band gap of photocatalyst is important factor in the use of semiconductor as a photocatalyst. The capacity of semiconductor photocatalyst to photoexcite electron from valence band to conduction band and separation of these charge carriers depend on the bandgap energy [19]. The demineralization through redox reactions of organic species adsorbed at the surface of the photocatalyst is governed by the reduction potential at conduction band and oxidation potential at valence band. If the redox potential of $H_2O / {}^{\bullet}OH$ is present within the bandgap domain of semiconductor then the semiconductor will act as a semiconductor photocatalyst. The band gap position of various semiconductor photocatalysts is shown in Fig. 2.

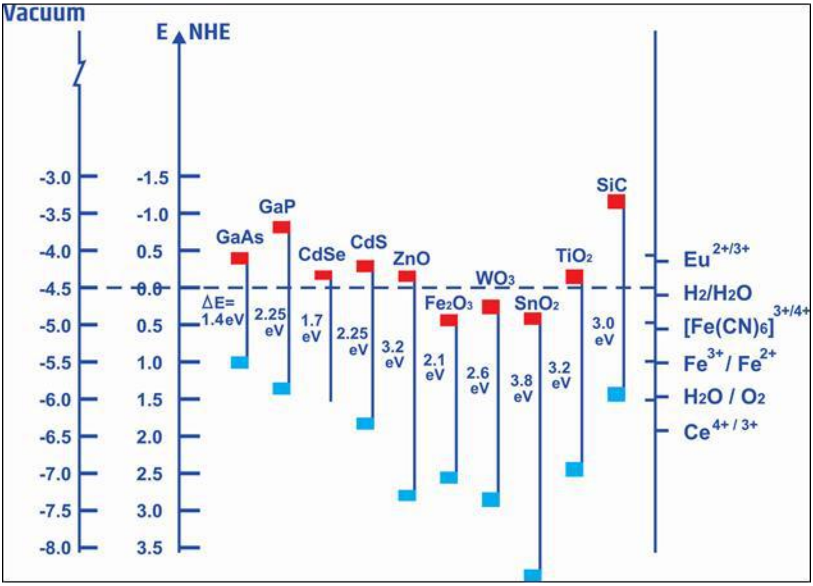

Fig 2: The band gap position of semiconductor photocatalysts

There are few criterions for a semiconductor to act as a good photocatalyst

i) It should be photoactive in visible and near visible light region.

ii) It should be biologically and chemically inert.
iii) It should be photostable.
iv) It should be inexpensive.
v) It should be non-toxic.

It is commonly observed that the p-type semiconductor photocatalysts having low bandgap energy can easily photoexcite electron from valence band to conduction band [20]. Since this p-type semiconductor photocatalyst show photoanodic corrosion so these semiconductors are quietly used as a photocatalyst. It is also observed that although n-type semiconductor photocatalysts have wide bandgap energy and they do not show photoanodic corrosion so usually used as a photocatalyst.

As shown in Fig. 2. most of the semiconductors have enough bandgap energy so they could show both oxidative as well as reductive reaction under the irradiation of UV and visible light. In spite of this, semiconductor like ZnS is unstable and show photoanodic corrosion while α-Fe_2O_3 shows photocathodic corrosion. While semiconductors like SnO_2, ZnO and CdS are having bandgap energy 3.8, 3.2 and 2.25 eV, respectively, so they are photoactive in visible and near visible region. Additionally, these photocatalysts are having good opto-electronic properties, low cost and non-toxicity [21].

1.2.2 Advanced oxidation process

Generally it is observed that most of the toxic wastewater pollutants are chemically stable and not amenable to physical as well as biological process so the complete demineralization of these pollutants is difficult task. To solve this issue new, eco-friendly, green and powerful method i.e. Advanced oxidation process (AOP) have been developed by the researchers. Advanced oxidation process is the water treatment procedure used for the removal of organic pollutants through oxidation reactions by using $^{\bullet}OH$ radicals [22]. The principle of advanced oxidation process is based on in-situ synthesis of highly active and unstable hydroxyl radical ($^{\bullet}OH$) for the complete demineralization of organic pollutants and pathogens. Among other oxidizing species generated in AOP ($H_2O_2, O_2^{\bullet-}, O_3$) the $^{\bullet}OH$ due to its highly unstable nature results in nonselective, complete demineralization of organic species present in wastewater. The concentration of toxic contaminants can be reduced from thousands of ppm to 1-5 ppb. This highlights the use of AOP in the present era. The organic pollutants get converted into the stable inorganic compounds like CO_2, H_2O and salts. This is known as demineralization. The main objective of AOP is the reduction of the toxic contaminants present in wastewater to such extent that the purified water can be directly discharged into the nature. As can be seen from Table 3, the ${}^{\bullet}OH$ is the second strongest oxidant having 2.8 Vs NHE oxidation potential.

Table 3: Oxidation potential of oxidants

Species	Oxidation potential (V) vs. NHE
Fluorine	3.03
Hydroxyl radical	2.8
Atomic oxygen	2.42
Ozone	2.07
Hydrogen peroxide	1.78
Perhydroxyl radical	1.70
Permanganate	1.68

This potential is enough to demineralize the organic pollutants into innocuous carbon dioxide and water. The semiconductor photocatalysts show photoexcitation of electron from conduction band to valence band after absorption of light (hν ≥ Eg). These photoinduced e/h pair gets involved in several redox reaction

$$SP \xrightarrow{h\nu} SP(h^+ + e^-)$$

The interaction of these charged species with organic compounds in aqueous medium results in its decomposition.

$$e^- + O_2 \rightarrow O_2^{\bullet -}$$

$$h^+ + {}^-OH \rightarrow {}^{\bullet}OH$$

$$R - H + {}^{\bullet}OH \rightarrow R^{\bullet} + H_2O$$

$$R^{\bullet} + h^+ \rightarrow R^{+\bullet} \rightarrow Intermediates / Product$$

The $O_2^{\bullet -}$ further generates $HOO^{\bullet}$ which reacts with electron from H_2O_2. The H_2O_2 is acts as an electron scavenger and show enhancement in the reaction rate.

$$O_2^{\bullet -} + H^+ \rightarrow HOO^{\bullet}$$

$$HOO^{\bullet} + e^- \rightarrow HOO^-$$

$$HOO^- + H^+ \rightarrow H_2O_2$$

The AOP using hydroxyl radicals have been used since 19th century but its use in the wastewater treatment was first introduced by Glaze *et al.* [23]. He suggested that the maximum generation of $^{\bullet}OH$ radicals enhances the water purification process and defined it as an advanced oxidation process.

Advantages of advanced oxidation process:

i) AOP can demineralize the organic pollutants in an aqueous phase i.e. without changing the phase of pollutant and photocatalyst.

ii) Heavy metals can be eliminated by formation of precipitate.

iii) As the $^{\bullet}OH$ radical is a strong, nonselective oxidant so it can demineralize almost every organic pollutant present in wastewater.

iv) AOP do not introduce any toxic compound into the water.

1.2.3 Basic principle of semiconductor photocatalysis

Photocatalysis is the reaction in which photocatalyst absorbs UV/visible light of proper wavelength and accelerate a photochemical reaction. In last few decades, the semiconductor photocatalysis has been emerged as an exciting branch since it results in the complete cleanup of toxic contaminants present in wastewater without producing any hazardous waste. Usually different semiconductor photocatalysts like TiO_2, CeO_2, Fe_2O_3, ZnO, CdS, MoO_3, WO_3, ZrO_2, SnO_2 and ZnS have been used as a photocatalyst because of their distinct electronic structure and narrow band gap [24]. In the first step of semiconductor photocatalysis, the irradiation of photocatalyst with UV/visible light which have energy $h\nu \geq Eg$. This interaction results in the photoexcitation of electrons from valence band to conduction band and leaves hole in the conduction band. In this way the e/h pair get generate in the semiconductor photocatalyst (Fig. 3.) In the absence of scavengers these photoexcited e/h pair show recombination and stored energy get dissipated. While if the scavenger is available during photocatalysis shows trapping of e/h pair. Ultimately, the recombination of e/h pair gets prevented and subsequent redox reactions take place. For bulk semiconductor particles only one either electron or hole is available for photocatalysis. However, for the very small particle size semiconductor both electron and hole are available for the photocatalysis.

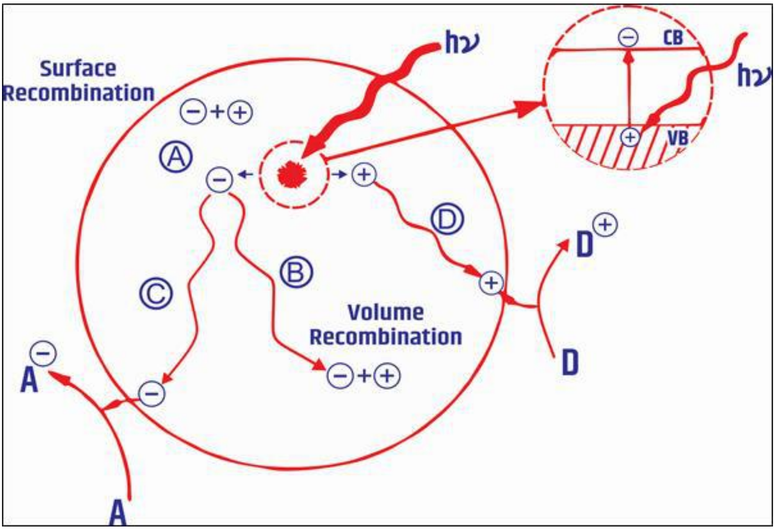

Fig 3: Schematic representation of photoexcitation-deexcitation pathway

Further these charge carriers follow different pathways. The photoexcited electrons from conduction band transfer to surface of semiconductor on which organic pollutants or solvent molecules are adsorbed. It is well known that electrons in conduction band are reducing agent and holes in valence band are act as oxidizing agent. If the continuum of mid gap states are less, the life of photoinduced charge carriers increases and initiates the redox process at the surface of semiconductor. The semiconductor photocatalysis is found to be productive when the recombination of photogenerated e/h pair is reduced. This can be accomplished by trapping of these either electron or holes.

The electrons present at the surface of semiconductor reduces the electron acceptor (O_2 to form superoxide radical $O_2^{\cdot-}$). While the holes migrate to the surface of semiconductor where holes oxidizes the electron donor (surface adsorbed H_2O or ^{-}OH oxidizes to $^{\cdot}OH$, H_2O_2 and $HOO^{\cdot}$ radicals). In the competition of these redox reactions at the surface of semiconductor, photogenerated charge carriers show surface and volume recombination with liberation of heat. The dissolved oxygen in aqueous medium is usually works as an electron acceptor and play vital role in semiconductor photocatalysis. Together these oxidation reaction at valence band and reduction reaction at conduction band result in the photoinduced demineralization of organic compounds into H_2O, CO_2 and mineral acids.

1.2.4 Mechanism in oxidizing species generation

The photocatalytic efficiency of semiconductor photocatalyst is depends on various interface charge transfer process which involves the e/h pair generation and recombination. This process generally occurs on the adsorbed phase. The photocatalysis is a complex sequence of reactions. Fig. 4. shows the redox reaction taking place in semiconductor photocatalyst.

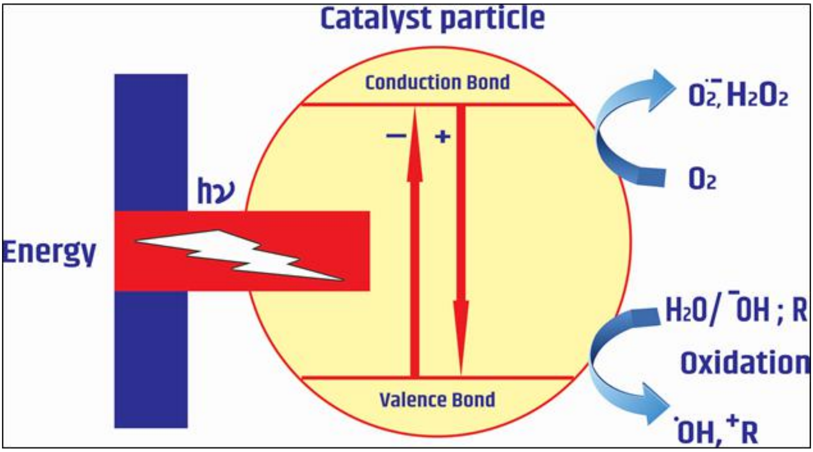

Fig 4: Schematic representation of redox reaction taking place in semiconductor photocatalyst

There are two different ways for generating $^{\cdot}OH$ radicals. The holes are either reacts with water molecules or ^{-}OH ions on the surface of the photocatalyst.

$$SP \xrightarrow{h\nu} SP\ (h^{+} + e^{-}) \rightarrow Recombination$$

$$h^{+} + H_2O_{ads} \rightarrow SP + {}^{\cdot}OH_{ads} + H^{+}$$

$$h^{+} + {}^{-}OH_{ads} \rightarrow SP + {}^{\cdot}OH_{ads}$$

It is also well known that O_2 plays a vital role in semiconductor photocatalysis.

Adsorbed O_2 can accept electron from conduction band to $O_2^{\cdot -}$ (superoxide ion). This $O_2^{\cdot -}$ ion further forms $^{\cdot}OOH$ and H_2O_2.

$$e^{-} + O_{2ads} \rightarrow O_2^{\cdot -}\,(Superoxide\ ion)$$

$$O_2^{\cdot -} + H^+ \rightarrow {}^{\cdot}OOH$$

$$e^- + O_2^{\cdot -} + H^+ \rightarrow H_2O_2$$

Accordingly, the synthesized H_2O_2 produces the active ${}^{\cdot}OH$ radical.

$$H_2O_2 \xrightarrow{h\nu} 2\,{}^{\cdot}OH$$

$$H_2O_2 + O_2^{\cdot} \rightarrow {}^{\cdot}OH + O_2 + {}^{-}OH$$

$$H_2O_2 + e^- \rightarrow {}^{\cdot}OH + {}^{-}OH$$

It is observed from above reactions that three electrons are required for the generation of one ${}^{\cdot}OH$ radical while only one hole is sufficient for the synthesis of ${}^{\cdot}OH$ radical. Therefore, most of the ${}^{\cdot}OH$ radicals are generated from holes. In most of the semiconductors the e/h pair recombination is high. Accordingly, the addition of some electron scavengers (O_2 molecules) shows the prolonging of e/h pair recombination and show smooth functioning of the photocatalysis. This is observed from above reactions that the adsorbed oxygen accepts electron from conduction band and get convert to superoxide ion ($O_2^{\cdot -}$). This reveals that the generation of highly reactive ${}^{\cdot}OH$ and demineralization of organic pollutants is not possible without water molecules.

The ${}^{\cdot}OH$ radicals are generated from the oxidation of adsorbed water molecules and adsorbed ${}^{-}OH$ ions in the demineralization of organic wastes. This demineralization proceeds through various oxidation, reduction and free radical reaction resulting into the synthesis of CO_2, H_2O and inorganic ions.

1.3 Semiconductor Photocatalysis and Literature review

1.3.1 SnO$_2$ as a photocatalyst

The photocatalytic degradation of organic pollutants using SnO$_2$ as a semiconductor photocatalyst is known to be a promising technology for wastewater treatment [25]. SnO$_2$ is an n-type photocatalyst and oxygen vacancies are its characteristic properties. As it has bandgap of 3.6 eV, the light with 350 nm wavelength is required for activation of photons. The modification in the structure of SnO_2 can decrease this wide bandgap. Accordingly, it results in the decrease in e/h pair recombination and increase more response towards visible light range [26].

1.3.2 SnO_2 -photocatalytic activity

The high rate of e/h pair recombination and high activation energy limits the commercial application of SnO_2 as a semiconductor photocatalyst [27]. For its commercial application its photocatalytic efficiency should be enhanced. There are several strategies for bandgap engineering like doping, co-doping, coupling etc. [28]. The doping improves the photocatalytic efficiency of semiconductor photocatalyst by decreasing the activation energy and e/h pair recombination. However, the methods used for the photocatalyst preparation and other parameters influences its efficiency. Therefore, the temperature, pH and frequency of irradiating light these factors are important and need to be studied during preparation of photocatalyst.

1.3.3 Improving photocatalytic activity by selective doping on SnO_2

1.3.3.1 Doping of SnO_2 with transition metals

For the effective degradation of organic contaminants in wastewater, the doping of semiconductor photocatalyst with transition metal ions is found to be a promising way [29]. Till this date many researchers have doped metal ions on SnO_2 to improve its visible light harvesting efficiency. The doping of SnO_2 with Co, Fe, Ag, Au and Mn are commonly studied [30]. Guang and coworkers has found that the photocatalytic efficiency of doped SnO_2 is depends on the temperature during the calcination process. The photocatalytic activity is observed to be decreased as the calcinations temperature increases. Anandan and coworkers confirmed that the doping of Mn^{2+} or Ce^{3+} increases the oxygen vacancies of SnO_2 which results in the improvement in its photocatalytic efficiency [31-32]. Cho and his group used Ag for the doping of SnO_2 along with electrochemically active biofilm. As compared to pure SnO_2, zinc metal ions doped SnO_2 nanorods showed improved photocatalytic dye degradation efficiency to that of pure SnO_2 nanorods.

1.3.3.2 SnO_2 doped with non metals

Behtash and coworkers observed that the typical n-type activity and improved charge density for Sb doped SnO_2 [33]. F-doped SnO_2 shows improved electronic conductivity and stability than that of pure SnO_2. Seema *et al.* successfully synthesized the graphene/SnO_2 composite with enhanced electrical conductivity and photocatalytic dye degradation efficiency [34]. The nonmetal ions doped SnO_2 shows light absorption in the range of 400-550 nm and the efficient organic contaminants degradation present in wastewater [35]. As the doping on the SnO_2 increases, enhancement in its photocatalytic efficiency is observed [36].

1.3.3.3 SnO_2 doped with rare earth metals

Reszczynska *et al.* showed that the smaller particle size of doped SnO_2 photocatalyst which results in enhancement in the photocatalytic efficiency [37]. In addition to this, lower the rate of e/h pair recombination results to be more efficient photocatalyst [38]. The rare earth metals doped SnO_2 semiconductor photocatalyst shows satisfactory photocatalytic properties as compared to pure SnO_2 in the visible range [39]. Al-Hamdi and coworkers revealed that the lanthanum doped SnO_2 photocatalysts are observed to be highly efficient to that of pure SnO_2 [40].

1.3.3.4 SnO_2 doped with other photocatalysts

The coupling of SnO_2 with other metal oxide semiconductor photocatalysts significantly inhibit the photoexcited e/h pair recombination [41]. Mostly SnO_2 is coupled with TiO_2 semiconductor photocatalyst. In the coupled nanocomposite the photoexcited electrons transfer from CB of TiO_2 to CB of SnO_2 and simultaneous transfer of holes from VB of SnO_2 to VB of TiO_2. This results in the successful separation of charge carriers and inhibits e/h pair recombination [42]. TiO_2-SnO_2 nanocomposite showed enhanced photodegradation of rhodamine B compared to pure SnO_2 and pure TiO_2 [43]. Cr_2O_3-SnO_2 nanocomposite also showed efficient photodegradation in visible light [44]. Zhang and coworkers reported that the particle size of nanocomposite is depends on the calcination temperature and metal oxides coupled nanocomposite shows increased photocatalytic activity compared to semiconductor also [45].

1.4 Role of activated carbon as a support

Semiconductor photocatalysts usually show demineralization of organic and inorganic pollutants present in wastewater when it is irradiated with UV and solar light. However, it is observed that during the photoinduced demineralization process, the interaction of pollutants and its intermediates cause the coagulation of powder semiconductor photocatalysts. Accordingly, the surface area of the photocatalysts gets decrease and it reduces the interaction of UV/visible light with pollutants. This results decrease in the photocatalytic efficiency of semiconductor photocatalysts [46].

Several scientists are working in this field to solve this coagulation issue by using different support materials to semiconductor photocatalysts. Various supporting materials like cellulose membrane [47], zeolites [48], ceramics [49], alumina clay [50], mesoporus materials [51] and glass bed [52] etc. have been used to reduce the coagulation problem.

There are few criterions for the optimum use of photocatalyst support.

i) The photocatalyst support must have high surface area.
ii) The photocatalyst support should be reusable with easy recovery.
iii) It should be chemically inert.
iv) The photocatalyst support should be strongly bonded with the semiconductor photocatalyst.

1.4.1 Activated carbon

Activated carbon (AC) is an amorphous, porous solid synthesized from lignite coal, woods and coconut shells [53]. Due to low cost, good adsorption capacity, high surface area (500-1000 m^2gm^{-1}) and porosity of AC, it is usually used as an adsorbent in the wastewater treatment. AC is also used for taste, colour and odour removal from drinking water. In addition to this several other factors like particle size, surface chemistry, contact time, temperature and pH affect the dye adsorption efficiency of active carbon [54]. Therefore, active carbon can play vital role in physico-chemical wastewater treatment and dye demineralization process.

1.4.2 Activated carbon supported photocatalysts

Among all the carbon based materials (CNTs, graphene, C_{60} and activated carbon) AC is tremendously researched as a support for semiconductor photocatalysts. Easy separation of active carbon from wastewater, easy availability, low cost, high adsorption capacity and porosity these factors attracted researchers towards active carbon.

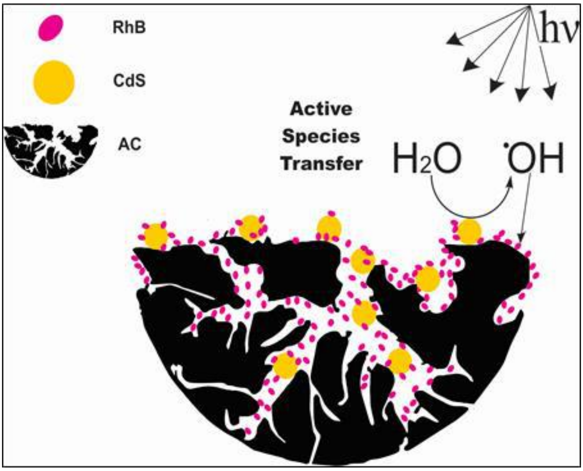

Fig 5: Mechanism of degradation of RhB using AC/CdS photocatalyst

Besides being only used as a semiconductor photocatalyst support the combination of photocatalyst and AC results in enhancement in photocatalytic efficiency of photocatalyst. It ultimately functions as a catalyst for wastewater treatment. Generally, the semiconductor photocatalysts get impregnated on the surface of active carbon. This is dispersed in aqueous medium containing pollutants.

The organic pollutants get adsorbed on the surface of activated carbon on which the semiconductor photocatalyst is already loaded as shown in Fig. 5. This results in the formation of interface between the organic pollutant and the photocatalyst. This loaded photocatalyst after UV-visible light irradiation generates e/h pairs. These photo induced e/h pairs further produces hydroxyl radical ($^{\bullet}OH$) i.e. reactive oxygen species. These $^{\bullet}OH$ present over the submillimeter periphery of the irradiated photocatalyst and it can demineralize the organic pollutants [55]. This results in the photodegradation of pollutants those are adsorbed on the surface of activated carbon and semiconductor photocatalyst. This adsorption process and production of $^{\bullet}OH$ on the periphery of the photocatalyst loaded activated carbon exhibit synergism and results remarkable enhancement in the photoinduced dye degradation of organic pollutants. In this mechanism active carbon play an important role as a photocatalyst support as well as it promotes the photocatalytic process. Active carbon provides common interface contact between active carbon and semiconductor photocatalyst. This results in synergistic effect. As the AC having all these benefits for semiconductor photocatalyst along with low market cost, high adsorptivity, non-polar and inert nature urged us to use it as a support for the semiconductor photocatalysts.

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