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website:- www.journalofchemistry.org**Synthesis and Applications of Nickel Nanoparticles
(NiNPs)- Comprehensive Review**Md. RAKIB HASSAN¹, FARHANA YASMIN¹, FATEMA KHAYRUN NOOR¹
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Chittagong Laboratories (Bangladesh)*Corresponding Author Email: sbhowmik.acce@nstu.edu.bd<http://dx.doi.org/10.22147/juc/190102>**Acceptance Date 2nd January, 2023, Online Publication Date 27th February, 2023****Abstract**

Nickel nanoparticles (NiNPs) have been the subject of extensive research over the past decade for a wide range of possible applications due to their exceptional strong catalytic activity, high compressive strength, free radical scavenging, and antibacterial property. In consequence of this, there has been a significant advancement in the methods of producing NiNPs, as well as in the suggested reaction processes and applications of these particles. The production, reaction mechanisms, and practical uses of NiNPs are reviewed in this work. NiNPs with sizes ranging from 1 to 100 nm can be manufactured in a number of different ways for use in both scientific and commercial contexts. Synthesis methods are divided into two categories: top-down methods and bottom-up methods which are subdivided into physical, chemical, and biological strategies. Extensive description has been given for the chemical processes involved in the creation of NiNPs, in particular those involved in biosynthesis approaches. The latest developments in the use of NiNPs in industries such as biomedicine, dye absorption, catalysis, supercapacitors, and dye-sensitized solar cells are reviewed. This work also provides examples of the benefits and functions of NiNPs in catalyzing various processes.

Key words : Nanoparticles, Biomedicine, Catalysis and Solar Cells.**1. Introduction**

Nanotechnology is the manipulation and

making materials at atomic and molecular level
of dimension 1-100 nm (at least in one dimension)

which have novel properties appreciably distinctive from their bulk counterparts¹. The building blocks of nanotechnology are nanoparticles². Nanomaterials have been used in different sectors such as chemistry, physics, biology, medical science, textiles, material science. Nanomaterials have been investigated extensively due to their unique optical, magnetic, electrical properties, high mechanical strength etc. and excellent for use as catalysts due to their enhanced surface area to volume ratio³⁻⁷. Different kinds of nanomaterials such as inorganic, carbon, organic based, metallic and nonmetallic nanomaterial, core-shell nanomaterials, composites, and metal oxide nanoparticles has already been synthesized^{8,9}. Among these nanomaterials, NiNPs gained much attention for different purposes such as catalyst, sensors, antimicrobial agents, anode, coating materials, magnetic fluid, propellant, sintering additives, adsorption of yellow dyes¹⁰, enhanced pseudo-capacitance¹¹, novel ink for nanotube-printing¹², battery manufacture *etc.*^{9,13}.

Nickel is a transition metal having atomic number 28, atomic mass 58.6934 and density 8.902 g/cm³ at 25°C. It has unique properties such as good ductility, malleability, high thermal, electrical conductivity, high mechanical strength, extraordinary corrosion resistance, low chemical resistivity, high reactivity, operational simplicity, eco-friendly *etc.* For the abovementioned properties, NiNPs become a promising material in the various branches of science¹⁴⁻¹⁶.

NiNPs are synthesized by various techniques typically physical methods, biological methods and chemical methods¹⁷. However, synthesis of NiNPs is much more complex due to their tendency to easily oxidized in air to form NiO, Ni₂O₃, Ni(OH)₂ or NiOOH, also including the difficulty of reducing Ni(II) to Ni(0) at room temperature^{18,19}. To avoid this difficulty, an inert

atmosphere during the synthesis is maintained or conducted under air-free condition using vacuum or inert gases or autoclave²⁰⁻²³. During microwave-assisted synthesis, the magnetic characteristics of NiNPs interfere with the magnets. Because of this, getting a high yield of the NiNPs is challenging²⁴. Due to their magnetic characteristics, NiNPs tend to cluster on formation, making it difficult to create monodispersed NiNPs²⁵. To prevent NiNPs from turning into Ni oxides or hydroxides, characterizing them as soon as possible after manufacture is essential. These considerations are essential for the synthesis of NiNPs²⁶.

In this review, we first introduce various methods of synthesis, reaction mechanisms. Furthermore, the application of NiNPs in various fields of nanotechnology, science, and biomedical sciences as well as the applications of NiNPs as catalysts in various fields are also discussed. This review also focused on recent techniques in the synthesis of NiNPs, ranging from green chemical methods to physical methods; in addition, to discuss the reaction mechanisms leading to the formation of NiNPs, as proposed and reported in recent literature and also the applications of only NiNPs, not nickel oxides and alloys.

2. Methods of synthesis of NiNPs :

Several methods have been developed to synthesize NiNPs with controlled size and shape. In the last few years, nickel nanomaterials with the following shapes have been synthesized: nanotubes, nanorods, hollow spheres, nanobelts, nanoprisms, and hexagonal flakes²⁷⁻³¹. Top-down synthesis methods and bottom-up synthesis protocols two traditionally adopted methods for the synthesis of NiNPs. The principal difference between the methods is the starting material or precursor used for the preparation of nanomaterials³².

2.1. Top down methods: In this method, preparation of NPs is based on the conversion of bulk material into small nano-sized particles by different physical and chemical treatments³³. It includes methods such as mechanical milling, thermal decomposition, nanolithography, and laser ablation³⁴. The main advantages of top-down methods are the cost and controlled shape and size of the product, ease to perform and are suitable for large scale production. The major problem associated with this method is the change in surface chemistry and physicochemical properties of NPs and not a suitable method for preparing informal shaped and very small size particles³².

2.2. Bottom up methods: This method of nanoparticle preparation is based on the formation of NPs from smaller molecules, such as the joining of atoms, molecules, or small particles³⁵. Generally, bottom-up methods are more advantageous than top-down methods in nanofabrication. The main advantages of this low-cost production method are the high precision in designing the size and shape of particles with a wide range of production of particle size and shape. However, this method is highly specific and difficult in large scale production³⁶. Top-down and bottom-up methods can be categorized into three main branches: physical, chemical, and biological methods for synthesizing NPs.

Physical methods :

In this method, bulk material is smashed into smaller parts by a big tube furnace. So top-down strategy mostly falls under this method³⁷. It avoids NPs solvent contamination but consumes a large quantity of energy for condensation and evaporation of particles and thus increases the cost of synthesis³⁸.

Chemical methods :

Chemical methods mostly follow the bottom-up strategy where NPs are synthesized to the required material from smaller molecules and sometimes combined with the capping agent for NPs synthesized stabilizing purposes. Compared to the physical technique, this method response is fast and cost-effective and highly pure and stable NPs can be synthesized by using reducing agents and protective agents. However, strong chemical can contaminate and associate with danger in the toxicity of the synthesized NPs and it is hard to regulate the variation in size and shape without significant reduction and stabilization of agents³⁹.

Biological methods :

Biological method is also categorized under bottom-up method where biological sources like plants, bacteria, fungi, and other microorganisms are used for the synthesis of NiNPs. It is known as biosynthesis or green synthesis where biomolecules combine with metallic substances to create NPs. It is a simple, ecological and stable technique⁴⁰.

NiNPs are synthesized by top down and bottom up methods. Top down methods include physical methods whereas bottom up methods include chemical and biological methods for synthesis of NiNPs. Physical methods include pulse laser ablation, mechanical milling, arc discharge and pulsed electrical spark discharge method. During the synthesis of NiNPs by biological methods, bacteria, fungi and plants extract are used. Chemical methods for the fabrication of NiNPs are chemical reduction, electrothermal, thermal decomposition, sol-gel technique, chemical vapor deposition, microwave, microemulsion and sonoelectrochemical method. Each process has some advantages as well as

Table 1. Various synthesis methods for NiNPs
Nickel Nanoparticle Synthesis

	Top down methods	Bottom up methods	
	Physical	Chemical	Biological
Methods	Mechanical milling, Pulsed electrical spark discharge, Arc-discharge method and Pulse laser ablation method.	Chemical reduction, Electrochemical, Thermal decomposition, Sol-gel technique, Chemical vapor deposition, Microwave, Microemulsion reduction, Sonochemical method.	Plant extract Bacteria, Fungi, Algae, Yeast

some drawbacks. In addition, the morphology and particle size distribution of the NiNPs depend on the applied synthesis method. Therefore, synthesis methods are chosen considering the nanoparticle size distribution, morphology, size, production cost, percentage of yield and hazard³⁴. Following Table 1 displays the various synthesis methods for nickel nanoparticle fabrication.

2.3. Physical methods :

2.3.1. Pulse laser ablation method :

Pulse laser ablation is a physical synthesis method for the fabrication of small sized NPs, which is carried out in a vacuum chamber in the presence of inert gas or liquid. It is a simple stable synthesis and “green” technical method that normally operates in water or organic liquids under ambient conditions⁴¹. NPs formed in this process via three steps: 1. generation, 2. transformation and 3. condensation of plasma mass. Several parameters such as time duration of laser pulse, wavelength, ablation time, laser fluency and effective surrounding liquid medium with or without surfactant influences ablation efficiency and characteristic of metal particle formed⁴². This method is a simple and effective technique for the formation of large amounts of NPs in the form of suspension and their properties can be changed accordingly selecting the laser parameter and nature of liquid. But some drawbacks are also

included due to the fact that prolong time laser ablation leads to formation of high amounts of NPs in the colloidal solution which block the laser path and also laser energy is get absorbed by already formed NPs instead of target surface which leads to a reduction in the ablation rate⁴³. NiNPs are also fabricated through pulse laser ablation or deposition method^{41,44}. For instance, Sakiyama *et al.*, fabricated NiNPs using Nd. YAG laser method with pressure, temperature and particle size of 1kPa, 400-800 °C, 5-20 nm respectively⁴⁵. In another study, Ganjali *et al.*, synthesized spherical NiNPs of 10nm using pulse laser ablation with wavelength, power and fluence 1070 nm, 0.4 W and 4.8 J/cm² and 30 mL of acetone⁴¹.

2.3.2 Mechanical milling :

Mechanical milling is a cost effective top down method of NP fabrication. The main objective of milling is to reduce the particle size and blending of particles in new phases. In this method, the powder mixture placed in a ball mill is subjected to high-energy collisions with the balls. Numerous ball mills of various capacities are available such as attrition ball mill, planetary ball mill, vibrating ball mill, low energy tumbling mill and high energy ball mill⁴⁶. Zhang *et al.*, synthesized spherical shaped NiNPs of 35-85 nm at 750 °C⁴⁷.

2.3.3. Arc discharge method :

NiNPs can be prepared by a top-down approach using an electric arc discharge and they have the potential to be applied as catalysts on a large scale. This method is advantageous as it is an environmentally friendly technique which continuously produce NPs of high purity. In this method, a controlled electric arc discharge between two Ni electrodes generates a plasma, which disintegrates the Ni to form NPs in deionized water⁴⁸. Fengmei *et al.*, synthesized spherical NiNPs of 20, 33, and 63 nm, corresponding to the diffuse, multiple, and constricted arc-anode attachments where the arc was formed for 12 min in Ar at pressure 101.325 kPa and the arc current and electron gap distance was controlled at 100 A and 6 mm respectively⁴⁹.

2.3.4. Pulsed electrical spark discharge :

Nanoparticle synthesis by electrical discharges in liquids is considered an efficient and ecological technique. Spark discharges between metallic electrodes immersed in distilled water are used to synthesize NiNPs. When mixed electrodes

are used such as Co-Ni or Ni-Co, both Co and Ni nanoparticles are produced, and the major species is dictated by the nature of the anode pin. The characteristics of NPs synthesized are analyzed under varying conditions of pulse width and voltage amplitude. Merciris *et al.*, synthesized square shaped NiNPs of 20nm when analyzed at pulse width and voltage amplitude of 5 kV and 100 ns respectively⁵⁰.

2.4. Chemical Methods :

2.4.1. Chemical Reduction Method :

Chemical reduction technique for the synthesis of NiNPs is one of the easiest methods in low temperature ranges. In this technique, Ni salt is reduced to NiNPs by various reducing agents such as primary amines, organic amines hydrazine hydrate, sodium borohydride *etc.*⁵¹⁻⁵⁶. In addition, different types of solvents such as Ether, polyols like ethylene glycol, diethylene glycol and triethylene glycol can be used^{56,57}. Sometimes, capping agents are used to prevent agglomeration of the particles, also to prevent from any unwanted environmental attacks like oxidation and such agents are polyvinyl pyrrolidone (PVP)^{58,59},

Table 2. Physical methods for the fabrication of Nickel Nanoparticle with working conditions and Morphology followed by product size

Method	Material	Morphology	Size	Ref.
Pulse laser ablation method	Nickel powder, acetone, fiber pulsed laser.	Spherical	10 nm	[41]
Mechanical Milling	Nickel sulfate hexahydrate (NiSO ₄ ·6H ₂ O), sodium hydroxide (NaOH), sodium chloride (NaCl).	Spherical	35-85 nm	[47]
Arc discharge method	Circular plate, Wire.	Spherical	20 nm	[49]
Pulsed electrical spark discharge	Nanosecond positive polarity pulsed power supply, high-voltage probe, current monitor, electrode configurations, quartz cell,	Spherical	10 nm	[50]
		Square	20 nm	
		Core-shell	50 nm	

sodium dodecyl sulfate, cetyltrimethylammonium bromide⁶⁰ *etc.* The growth, crystal structure, morphology, shape, size of NiNPs synthesized by chemical reduction method depend on the concentration of reducing agent, molar ration of reducing agent to precursor, temperature, solvent, nature of Ni precursor⁵¹. The Crystal size of the NiNPs increase with a decrease in the molar ratio of reducing agent to precursor and decreases with an increase in the molar ratio⁵². The NPs structure depends on the molar ratio of reducing agent to precursor, with amorphous structure forms in lower molar ratio and crystalline structure in higher molar ratio⁵¹. The major problem arise during synthesis is the control over their size to provide homogeneity, which can be solved by adding capping agents like PVP⁶¹. For instance, Ankur *et al.*, reported that NiNPs was successfully synthesized utilizing hydrazine hydrate and polyvinyl pyrrolidone (PVP) as reducing agent and capping agent respectively at 60 °C for 1 hour. The size of NiNPs synthesized by this process is about 12 nm⁵¹.

2.4.2. Electrochemical Method :

Electrochemical method for the synthesis is a simple, fast, environment friendly, allows precise control of the erosion of the electrodes and control of the nanoparticle size, which is carried out at room temperature. In this method, NiNPs were synthesized using an electric discharge, improved by a computerized control implemented with virtual instrumentation⁴⁸. A plasma has been generated between two nickel electrodes by a controlled electric arc discharge, disintegrates rapidly to form NPs in deionized water. A wire having a cross-section of 0.70 mm x 0.25 mm and a circular plate having diameter of about 12 mm and thickness of 5 mm, both composed of 99.9% nickel, used as the anode and cathode respectively. The particle size varies with

the voltage applied^{48,61}. Rogelio *et al.*, reported that, at an open circuit voltage of 30 V 50% of the NPs are smaller than 27 nm, while at 80 V, they are less than 15nm and at 6 A and 80 V most of the NPs are smaller than 15 nm. Thus, the nanoparticle size decreased with increasing voltage^{48,62,63}.

2.4.3. Thermal Decomposition :

In this method, endothermal chemical decomposition occurs where heat is generated and breaks the bonds in the compound. The specific temperature at which an element chemically decomposes is termed as decomposition temperature. Hence, by decomposing the metal at its decomposition temperature, undergoing a chemical reaction producing NPs⁶⁴. The size of the particle increases with increase in the concentration of nickel salt solution. This method has some advantages such as simple process, low cost, and easiness to obtain high purity products; hence it is quite promising and facile route for industrial applications. Z. Fereshteh *et al.*, used nickel octanoate Ni(octa)₂ as precursor and oleylamine (C₁₈H₃₇N) as stabilizing agent at 240 °C for 45 min during the thermal decomposition synthesis of spherical NiNPs of 25 nm⁶⁵. Figure 1 shows a scheme of thermal decomposition techniques to produce NiNPs⁶⁶.

2.4.4. Sol-gel technique :

This technique involves a colloidal solution of solids suspended in a liquid phase termed as the sol and a solid macromolecule submerged in a solvent termed as the gel. This technique is the most preferred chemical technique due to its accuracy, stability, low reaction temperature, and a high purity of targeted products and simplicity. This is a wet chemical process and the precursor is a chemical solution which contains an integrated



Figure 1: Thermal decomposition techniques to produce NiNPs⁶⁶.

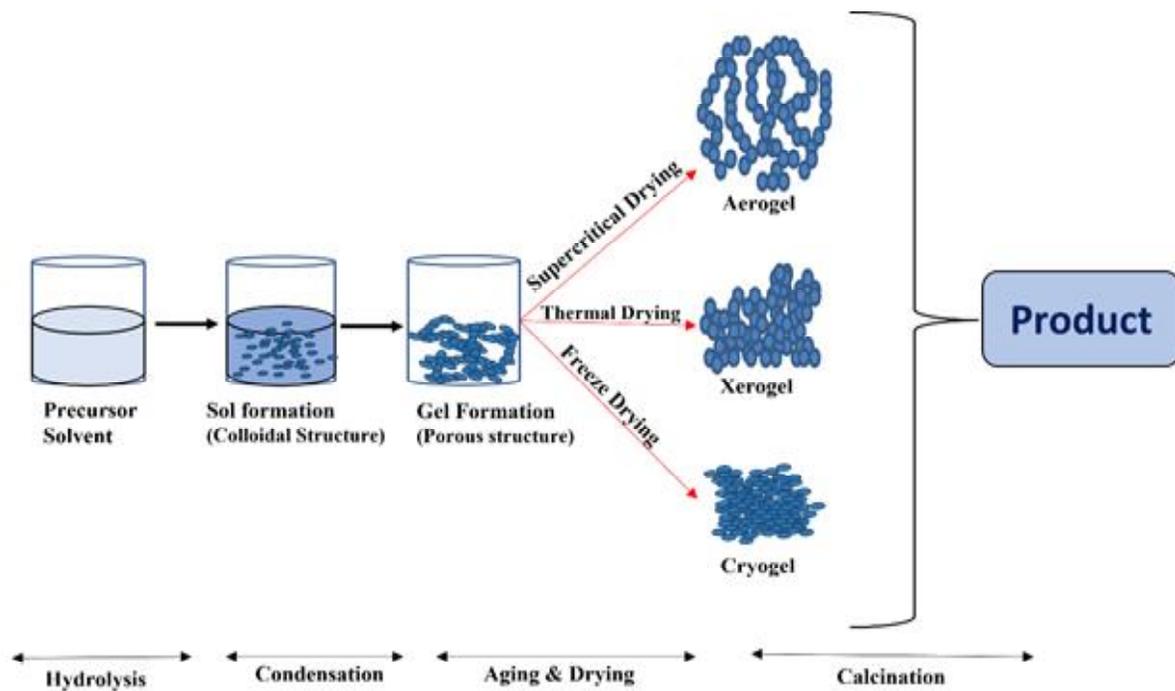


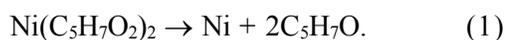
Figure 2: Sol-gel Technique⁶⁸.

system of discrete particles. Jaji *et al.*, maintained the solution at pH 11 and the calcination temperature at 450 °C. Before calcination the particle was in amorphous phase and after calcination, a cubic structure was present. The cubic structure of NiNPs formed with an average diameter of approximately 32.9 nm^{67,68}. Aisha *et al.*, used aqueous solution of nickel nitrate hexahydrate converted to green precipitate at pH 11 which was dried and calcined at 550 °C for 3 hours during the sol-gel synthesis of NiNPs of 40-45 nm⁶⁹.

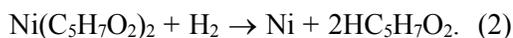
2.4.5. Chemical vapour deposition (CVD) technique :

This technique includes a thin film of gaseous reactant deposited onto a substrate. In the reaction chamber, the combination of gaseous molecules occurs at ambient temperature. The heated substrate then undergoes a chemical reaction with the combined gas⁷⁰. A thin film of products deposited which is recovered and used. Substrate temperature is the influencing factor in this technique. The two precursor decomposition methods include thermal decomposition and reduction by hydrogen⁷¹.

1) Thermal decomposition in an inert atmosphere



2) Reduction with hydrogen



Advantages of this technique include the production of uniform, highly pure, hard, and strong NPs and the disadvantages include highly toxic gaseous by-products and the prerequisite of unique equipment⁷⁰. Pavel *et al.*, synthesized NiNPs of 10-15 nm by chemical vapor deposition of nickel acetylacetonate in an externally heated tube flow reactor at 500 °C⁷¹.

2.4.6. Microwave :

Microwave combustion technique is highly exothermic which provide uniform distribution of temperature within the bulk material and leads to the fast production of NPs. The microwave oven used is programmed in such a way that it led to the formation of NiNPs as the product. Advantages include that this technique is rapid and economic in terms of time, simplicity, and energy. Ragupathi *et al.*, used aluminium nitrate and nickel nitrate as precursors during the fabrication of NiNPs via microwave combustion technique⁷². LaGroq *et al.*, fabricated face centered cubic NiNPs by employing trioctylphosphine surfactants under a reducing hydrogen atmosphere and also found that changing the nickel precursor concentration to trioctylphosphine ratio can alter the face shape and size from spherical at 5 nm to cubic at 12 nm⁷³.

2.4.7. Microemulsion reduction :

Microemulsion reduction is a nanomaterial synthesis method in which chemical reduction takes place in an organic solvent in the form of microemulsion such as water in oil, oil in water, water in supercritical carbon dioxide. The two types of microemulsion system include micelles (oil in water) and reverse micelles (water in oil). Microemulsion (reverse micelles) method was used to synthesis NiNPs^{19,74}. Chen *et al.*, synthesized face centered cubic NiNPs of 4.6 nm¹⁹. Advantages of this process include more uniform size distribution of produced copper nanoparticles. However, main drawback of this process is high operation cost during the separation of solvent from product¹⁹.

2.4.8. Sonochemical method :

In sonochemical method, high frequency ultrasound (20 KHz to 10 MHz) is applied to the

electrolyte solution (nickel salt) during precipitation period in order to enhance chemical reduction process. This method is composed of three stages: first, the formation of nickel hydroxide precursor precipitate; second, ultrasonic irradiation, and subsequent transformation to NiNPs by heat treatment. Ultrasonic irradiation resulted in cavitation phenomenon and leads to decrease crystalline size of the NiNPs. Mohammadyani *et al.*, synthesized cubic NiNPs of 20nm by a novel sonochemical approach⁷⁵.

2.5. Biological Method :

2.5.1. Synthesis of NiNPs using plant extract:

Metal ions can be reduced to NPs using biomolecules found in plant extracts. Plant extracts have become increasingly popular as a result of the low cost, easy availability, and

compatibility of most plants⁷⁷. Plant extracts also contain several reducing and capping agents. As a result, NPs with a range of morphologies can be created using these methods. Because of its inexpensive cost and quick reaction time, phytochemical synthesis is always preferred for nanoparticle synthesis. For the creation of NiNPs, extracts from various sections of a plant, such as the stem, leaves, roots, and flowers, are mixed with Ni solution. To assist the creation of NPs, plant extract contains a reducing and capping agent⁷⁸. Biosynthesis is typically performed at room temperature, at an optimal pH, and with or without stirring. Plant extracts are used to mediate synthesis, which is environmentally friendly. Extracts from a wide range of plant species have been successfully used to make NPs.

Table 2: Chemical methods for nickel nanoparticles synthesis with reaction condition and product size

Method	Materials (Precursor)	Morphology	Size	Ref.
Chemical reduction	Nickel chloride hexahydrate,	Spherical	10-15 nm	[51]
Electro-chemical method	circular plate of 12mm diameter, 99% Ni used as anode and cathode respectively.	Spherical	15-27 nm	[48]
Thermal decomposition	Stainless steel tube	Face-centered cubic, spherical	20-25 nm	[66]
Sol-gel technique	Nickel (II) nitrate hexahydrate [Ni(NO ₃) ₂ ·6H ₂ O]	Cubic Spherical	32.9 nm	[76]
Chemical vapour deposition (CVD) technique	Ni-acetylacetonate	Face centered cubic, cubic	10-15 nm	[71]
Microwave	Nickel nitrate	Spherical Cubic	5 nm 12 nm	[73]
Microemulsion reduction	Nickel chloride	Face centered cubic	4.6 nm	[19]
Sonochemical method	Nickel nitrate, Ni(NO ₃) ₂	Cubic	20 nm	[74]

Figure 3: Biosynthesis of NiNPs from Plant extract⁷⁶.

Table 3: Green reducing agents used for the synthesis of nickel nanoparticles

Green Reducing Agent	Portion of the plant	precursor	Morphology	Size	Ref.
<i>Lactuca serriola</i>	Seed	NiCl ₂ .6H ₂ O	Slightly spherical	<100 nm	[81]
<i>Citrullus Colocynthis</i>	Stem	Ni(NO)	Rectangular, triangular, spherical	60-100 nm	[10]
<i>Ocimum Sanctum</i>	Leaf	Ni(NO)	Slightly spherical	12-36 nm	[82]
<i>Desmodium Gangeticum</i>	Aquous root	NiCl ₂	Spherical	23 nm	[83]
<i>Psidium guajava</i>	Leaf	NiCl ₂ .6H ₂ O	Spherical	22-44 nm	[84]
<i>Medicago Sativa</i>	Alfalfa	Ni(NO ₃) ₂	Spherical	1-6 nm	[85]
<i>Aegle Marmelos Correa</i>	Leaf	NiCl ₂	Triangular	80-100nm	[86]

2.5.2. Synthesis of nickel nanoparticles using starch and plant secretion as reducing agent:

NiO nanoparticles were made from Arabic gum using the solvent–gel method. The method may be utilized to produce low-cost transition metals nanoparticles from their oxides and other materials⁷⁹. Starch can also be used to make nanosized nickel materials. Carbonization

in flowing hydrogen produces distinctive core–shell-structured NiNPs from starch and the metal salt⁸⁰.

2.5.3. Synthesis of NiNPs using microorganisms as reducing agent :

One of the most promising green synthesis strategies for NiNPs manufacturing is

the microbial method. In this method, biomolecules present in the microbe act as both reducing and stabilizing agents. The two categories of microbial synthesis methods are intracellular and exterior microbial synthesis methods. Metal ions are carried within the microbial cell and reduced to metal nanoparticles by enzymes in the intracellular method, whereas metal ions are absorbed on the cell surface and reduced to NPs with the help of enzymes in the extracellular method⁸⁷. In the synthesis of copper nanoparticles, bacteria, fungi, and algae are commonly utilized as microbes. There are three steps to this method: microbe culture, cell free metabolite isolation, and metal ion reduction.

2.5.3.1. Bacteria :

For the synthesis of NiNPs, different bacterial stains were utilized. Biomolecules serve as a reducing and capping agent in this situation. Bacteria are found to be promising microorganisms for the manufacture of NPs among all biological systems studied to date because culturing of bacterial stain is easy. Bacterial stains are able to

produce extracellular NPs with easy downstream processing since they are easy to grow. *Thermoanaerobacter ethanolicus* is used to synthesize NiNPs which has an octahedral morphology⁸⁷.

2.5.3.2 Fungi :

A variety of fungi were used to synthesize copper nanoparticles. They create a variety of extracellular enzymes that aid in the conversion of copper ions to copper nanoparticles. *Aspergillus terreus* strains encapsulated in polyurethane foam were used to make NiNPs replacing synthetic adsorbents with bio-adsorbents in the treatment of industrial waste is more feasible. Furthermore, the bioadsorbents can be recycled and are cheaper than synthetic resins⁸⁷.

2.5.3.3 Algae :

In benign settings, algae-derived phytochemicals are actively involved in bio-reduction and coating as-prepared NPs. Marine red algae extract is used to biosynthesize nickel oxide nanoparticles⁸⁸.

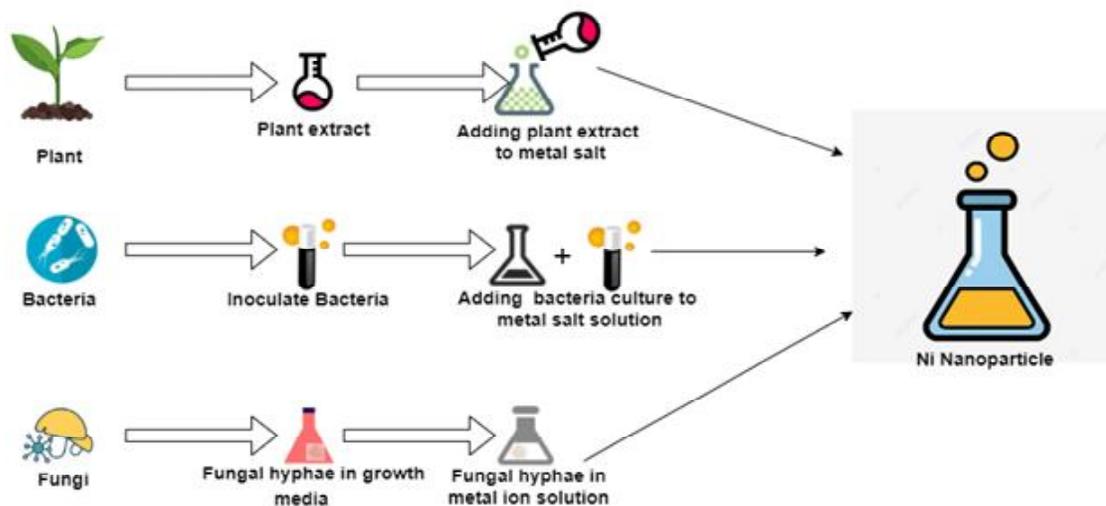


Figure 4: Outline of micro-organisms assisted metal nanoparticles synthesis method⁸⁶.

3. Applications of NiNPs :

3.1. NiNPs in biomedical applications :

NiNPs have the ability to deliver drugs and genes as well as various properties which include boosting cell permeability, promoting cellular absorption, anti-larvicidal efficiency, anti-inflammatory, anti-bacterial properties. It also has excellent catalytic and magnetic properties, colloidal stability, and antioxidant properties. These properties help NiNPs to be applied in various biomedical applications. Some of the examples include the Suppression of microbial pathogens such as *Staphylococcus aureus* and *Escherichia coli*, targeting leukemia cancer cells cytotoxicity, larvicidal efficiency against *Culex quinquefasciatus*, magnetic resonance imaging, and many more^{56,86,89-94}. NiNPs are extracted using *Lactuca serriola* was reported to have antibacterial activity against *Pseudomonas aeruginosa*, *Staphylococcus aureus*, *Staphylococcus epidermidis*, *Basilus subtilis*, *Basilus pumilus*, *Micrococcus luteus*, *E. coli*, and *Bordetella bronchiseptica* at low doses. At optimal conditions, practically total inhibition is achieved⁸¹.

Ivanov *et al.* recognized a synergistic impact between NiNPs and reduced graphene oxide, which paves the way for the development of high-performance applications in bioinspired microelectronics for medical therapy⁹¹. Angajala *et al.* shown that NiNPs have potent larvicidal efficiency against *Culex quinquefasciatus* and superior anti-inflammatory action, on par with that of a conventional treatment. They theorized that the NiNPs may be utilized not only as an effective medication carrier, but also for the prevention of lymphatic filariasis and dengue fever by reducing the prevalence of the mosquito-borne disease vector, *Culex quinquefasciatus*⁹⁵.

In another study, Helan *et al.* have

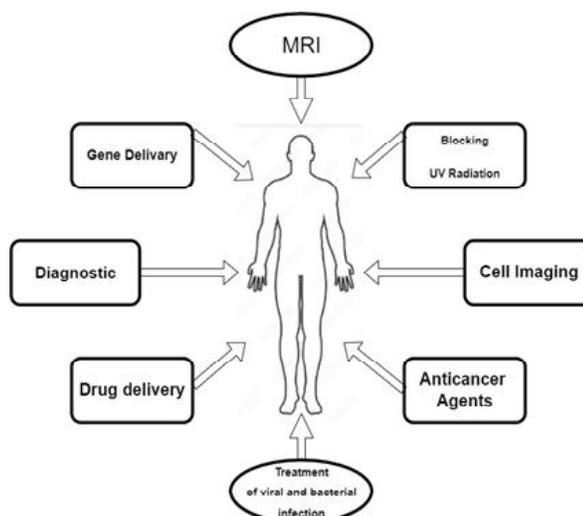
proposed NiNPs for use in preventing the spread of bacteria like *Staphylococcus aureus* and *E. coli*⁹⁶. Roselina *et al.* pointed out that NiNPs had exceptional catalytic and magnetic capabilities given its enormous potential in various applications, including biological and medicinal ones⁹⁷. Gong *et al.* found that algae not only convert NiO to Ni, but also speed up the aggregation of NPs. Bioremediation of nano-pollution with green algae was mentioned as a possible solution in their study [98]. According to research by Sudhasree *et al.*, green NiNPs have good antibacterial effects because they are colloiddally stable and have antioxidant properties⁹⁹.

NiNPs have the advantage of being applicable for both diagnostics and treatments, as demonstrated by an *in vitro* and *in vivo* investigation by Gorgizadeh *et al.* on melanoma tumors in a mouse model¹⁰⁰. Neiva *et al.*, synthesized NiNPs and were subsequently incorporated into electrodes for use as electrochemical sensors for glycerol, a relevant analyte with applications in the pharmaceutical, biofuels, clinical diagnosis, and food industries¹⁰¹. The electrochemical glucose sensor developed by Liu *et al.* demonstrates excellent sensitivity, attractive selectivity, low detection limit, broad linear range, attractive selectivity against common interferes in physiological fluids, high stability, and remarkable feasibility for real sample analysis¹⁰².

The use of NiNPs for thermotherapy was reported by Hoque *et al.* They showed that by adjusting the particle size, shape, magnetism, and concentration, the necessary temperature for hyperthermia heating could be adjusted¹⁰³. In another study, Ghaedi *et al.* have synthesized a new adsorbent for the quick and simultaneous removal of methylene blue (MB) and safranin-o (SO), two of the most frequently occurring chemicals in wastewater¹⁰⁴. Song *et al.* produced

Table 4: Biomedical application of nickel nanoparticles.

Application of NiNPs	Structure	Precursor	Size (nm)	Ref.
Sonodynamic cancer therapy	Colloidal	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	38.2	[100]
Electrochemical sensor for glycerol	HCP(elaboration)	$\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$	8.9	[101]
Electrochemical glucose sensor	FCC (elaboration)	Nickel acetate	15	[102]
Thermo-therapeutic application	Crystalline	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	28	[103]
Adsorption of methylene blue and safranin-o	Amorphous	$\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$	320	[104]
Hydrodeoxygenation of stearic acid and microalgae	Colloidal	$[\text{Ni}(\text{acac})_2]$	3	[90]
Anti-inflammatory and mosquito larvicidal efficacy	FCC	NiCl_2	80-100	[95]

Figure 5: Biomedical applications of NiNPs⁹⁷.

3 nm NiNPs and used them as a catalyst for the hydrodeoxygenation of stearic acid and microalgae oil, resulting in increased initial rates and increased stability⁹⁰.

3.2. Dye removal using NiNPs :

Many organic pollutants are entering the water supply as a result of the growing number of chemical businesses¹⁰⁵. The textile, paper, and leather industries are the main sources of dye,

which is a toxic organic pollutant. Dye is a colored organic molecule that is generally water-soluble from a chemical standpoint. Due to its possible negative features such as toxicity, carcinogenic nature, persistence in the environment, non-biodegradability, and others, it has detrimental effects on the environment¹⁰⁶. For the decolorization of the colorful effluent, metal nanoparticles are used. Decolorization is influenced by the size and shape of NPs, which can be adjusted through a variety of physical and chemical methods. The

following equation is used to calculate decolorization¹⁰⁷.

$$\% \text{ Decolorization} = \frac{(\text{Initial Concentration} - \text{Final Concentration})}{\text{Initial Concentration}} \times 100$$

3.2.1. Mechanism of dye removal :

NiNPs are activated by solar light where, electrons and holes are generated as a result of

solar light absorption. Superoxide radical and hydroxyl radical are formed when the generated electron and $\text{H}(\cdot)$ react with oxygen and water. The chemical reaction between dye and superoxide anion or hydroxyl ion causes dye to degrade through oxidation and reduction. A general degradation reaction and process is illustrated.

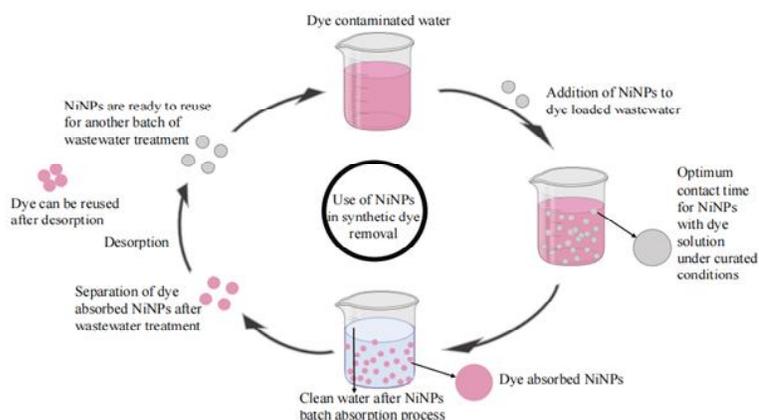
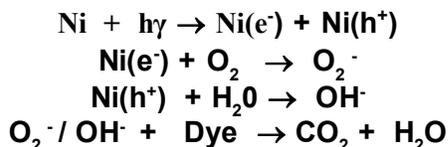


Figure 6: Mechanism of dye removal by nickel nanoparticle⁹⁴.

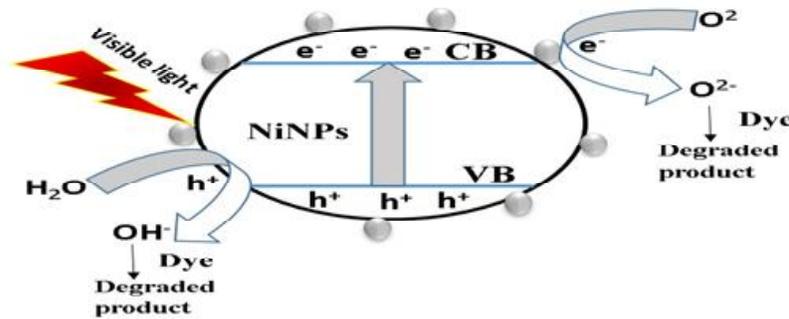
Magnetic metallic NiNPs are attractive candidates for the adsorption of dyes due to their high surface area. The elimination of organic dyes as important contaminants in wastewater makes the removal of dyes from wastewater an absolute necessity. Organic dyes cause a decrease in the quality of the water, which has serious repercussions for people's health. The vast majority of organic dyes are extremely dangerous. It was reported by Jin and colleagues that NiNPs were used for the separation of dyes from aqueous solution. They discovered that NiNPs that had a big pore volume and a high surface area were able to be easily isolated from the aqueous solution by using an external magnet⁹¹. NiNPs have been reported

by Ghaedi *et al.* to be a new adsorbent for the selective and competitive removal of methylene blue and safranin-o⁹⁵.

In addition, Sudhasree *et al.* reported the production of NiNPs that did not contain any surfactants. These NiNPs were then utilized in the process of removing Congo red, an azo dye, from industrial effluent⁹⁶. Zhang *et al.* verified the production of NiNPs with superior magnetic characteristics and crystallite sizes ranging from 10 to 30 nm. Following their synthesis, these NiNPs were put to use as adsorbents to remove Congo red from industrial wastewater⁹⁷.

Table 5: NiNPs used in the application of various dye removal.

Material	Precursor	Synthesis Method	Dye	Degradation %	Ref.
NiNP	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	Biosynthesis	Crystal violet dye	95	[81]
NiNP	$\text{Ni}(\text{NO}_3)_2$	Biosynthesis	Reactive yellow 160 dye	91.4	[10]
NiNP	$\text{Ni}(\text{NO}_3)_2$	Biosynthesis	Crystal violet (CV)	92	[82]
			Eosin Y (EY)	94	
			Orange a	91	
Ni/PC-CNT	Ni-ZnMOF	Chemical Synthesis	Malachite green (MG)	89.8	[108]
			Congo red (CR)	81.8	
			Rhodamine B (RhB)	39.5	
			Methylene blue (MB)	31.2	
			Methyl orange (MO)	27.1	
NiNP	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	Chemical synthesis	Congo red	96.67	[109]

Figure 7: Mechanism of dye removal by nickel nanoparticle in dye sensitized solar cells¹⁰⁸.

3.3. Use of NiNPs in dye sensitized solar cells and sensors :

Krishnapriya *et al.* have been successful in fabricating dye-sensitized solar cells while working with various nanostructured TiO_2 morphologies in a variety of solvents, as well as size and shape-tuned NiNPs consisting of mixed triangular and hexagonal morphological crystals and ranging in size from 15 to 62 nm¹¹⁰. A simple, efficient, and fast microwave-assisted solvothermal method was used to create NiNPs which could be used as photoanodes, and their shape is very unique. They found that by adding Ni nanocom-

posites, they were able to effectively trap incident light, which in turn increased the efficiency with which electron hole pairs formed and short circuit current was generated. After a month of exposure to standard electrolytes, the manufactured dye-sensitized solar cells showed no signs of degradation in performance.

In another study, a high-performance, nonenzymatic sensor based on a Ni nanoparticle-chitosan nanocomposite was created by Liu *et al.* They proposed using nonenzymatic sensors for blood glucose monitoring because of its inexpensive cost, easy fabrication, and efficient

detection of glucose³.

3.4. Applications of NiNPs as catalyst :

Due to the strong catalytic activity, great stability, and other desirable qualities, NiNPs have attracted a lot of interest in a variety of fields. Recently, NiNPs have been utilized to enhance CO₂ breakdown, even in unfavorable water chemistry conditions. NiNPs are superior to other catalysts for CO₂ hydration because their activity does not depend on the pH of the solution in contrast. Carbonic anhydrase and hypobromous, hypochlorous, and boric acids are significant catalysts but are less common as they work best in an alkaline environment¹¹¹⁻¹¹³. NiNPs, which are becoming increasingly popular as an alternative to the conventional Raney nickel catalyst, are attracting attention in organic synthesis because of their novel inherent features. As a catalyst, NiNPs have been put to use in a wide variety of functional group transformations, including those involving carbonyl compounds, aldehydes, thiols, ketone alkylation, and tetraketone synthesis¹¹⁴.

Under the same reaction circumstances, the NiNPs performed better as catalyst than other forms of nickel. Additionally, the NiNPs could be easily separated by decantation with an excess amount of 2-propanol and reused up to five times, keeping a high activity in a very simple reaction media consisting of the NiNPs, 2-propanol, and the substrate, with no base¹¹⁵. The existence of more regularly spaced, sintered, resilient NiNPs allowed the catalytic NiNPs to sustain a high degree of activity even after four cycles of reaction, as reported by Song *et al.*¹¹⁶. Separating emulsions, cleaning oil spills, purifying water, and isolating contaminants in samples are just some of the many applications for NiNPs as catalysts. The strong magnetic response and interfacial characteristics of NiNPs make them very useful

in effective adsorption and quick separation¹¹⁷. NiNPs are being studied as a potential non-precious metal catalyst in magnetic nanomaterials, biomedicine, and optoelectronics devices¹¹⁸. Several researchers have discovered that NiNPs can stand in for the more expensive noble metals during hydrogen transfer hydrogenation and hydrogen auto transfer processes. The reductive amination of aldehydes and transfer hydrogenation of olefins and carbonyl compounds using 2-propanol as the hydrogen donor were discovered to be catalyzed by these NPs¹¹⁹. NiNPs has tremendous potential in catalysis of hydrogen evolution processes in alkaline condition, as reported by Gong *et al.* Its activity equals that of the most efficient acid-catalyzed hydrogen evolution process¹²⁰. It was also discovered to be comparable to platinum-based catalyst. In addition, Feng *et al.* demonstrated that NiNPs serve as a catalyst for hydrogen evolution in addition to providing protection¹²¹. With 2-propanol as the hydrogen donor, Alonso *et al.* showed that NiNPs can efficiently catalyze the heterogeneous transfer hydrogenation of olefins¹²². To reduce 1-octene, Raney nickel and NiNPs both performed similarly, however the former required a longer reaction time to achieve the same conversion at 76 °C while the latter's activity reduced dramatically when cooled to room temperature. However, several commercially available nickel catalysts (Ni-Al, Ni/SiO₂-Al₂O₃, and NiO) were completely inactive under these conditions. The *r*-alkylation of ketones and the reductive aza-Wittig reaction, which produces secondary amines, were both made possible by the NiNPs. To our knowledge, this is the first time that a catalyst other than a noble metal has been used to accomplish either of these reactions¹¹⁵. As reported by Ragupathi *et al.*, benzyl alcohol can be selectively oxidized to benzaldehyde using NiNPs⁷². According to research by Saxena *et al.*, NiNPs can function as a green catalyst, catalyzing the selective oxidation

of various thiols to disulfides in a relatively short amount of time at room temperature with no byproduct formation¹²³. Dander and Garg found NiNPs to be effective catalysts for C-N bond breaking in amides, leading to a number of beneficial chemical reactions including esterification, transamidation, Suzuki-Miyaura couplings, and Negishi couplings. As they put it, breaking the C-N bond gives a new method to produce C-C bonds and C-heteroatom via amide¹²⁴. Cathode catalysts made from NiNPs have found application in microbial fuel cells (MFCs). For the first time, Ghasemi *et al.* looked into NiNPs as a feasible replacement for platinum in MFCs¹²⁵. Recent research has shown that NPs/straight multi-walled nano tubes have a significantly increased electrocatalytic activity under basic circumstances for the electro-oxide of glucose. For the purpose of studying glucose oxidation, Nie *et al.* constructed a nonenzymatic amperometric sensor based on NiNP/straight multi-walled nanotubes¹²⁶.

High activity and reasonable cost have led to Ni-based catalyst's recent inclusion among the several catalysts used to convert syngas to methane. As a means of reducing catalyst inactivation, the highly active, appropriate, and resilient Ni-based methanation catalyst developed by Kamata *et al.* consists of well-dispersed NiNPs contained in a mesoporous silica matrix prepared using a two-step co-precipitation process with high Ni loading up to 40%. In comparison to a commercially available supported Ni methanation catalyst, the as-synthesized catalyst exhibited significantly better Ni sintering, coking, and sulfur resistance¹²⁷. Li *et al.* produced the Ni/La₂O₃/SiO₂ methanation catalyst employing LaNiO₃ with a perovskite structure as the precursor loaded on mesoporous silica via the citrate complexing process¹²⁸. According to their report, the resulting catalyst was highly stable, highly active, and highly selective for CO methanation from syngas. NiNPs' high

stability is a result of their proximity to and confinement by La₂O₃ that has been dispersed on SiO₂, which makes them resistant to carbon deposition and, as a result of their interaction with La₂O₃, makes them resistant to sintering. For the conventionally impregnated catalyst, NiNPs and La₂O₃ are typically supported on different types of SiO₂.

3.5. NiNPs application as a high compressive strength material :

Objects of the micrometer or nanoscale can be significantly stronger than macroscopic ones, but they rarely demonstrate the maximal theoretical strength of the material. In a study, Sharma *et al.* showed that faceted single-crystalline NiNPs have a compressive strength of up to 34 GPa, which is extremely high for metallic materials. The existing estimations of Ni's theoretical strength are comparable to this strength. This unprecedented strength can be attributed to the combination of the significant Ni shear modulus, the rounded corners and edges of the NPs, and the thin oxide coating on the particle surface¹²⁹.

3.6. Application of NiNPs in electrochemical sensors :

NiNPs based electrochemical sensors rely on the catalytic oxidation of analytes by Ni³⁺ from an alkaline-generated redox pair of nickel (II) hydroxide (Ni(OH)₂) and nickel (III) oxide-hydroxide (NiOOH)^{101,130}. Due to its stability, this redox reaction can only take place in a very alkaline medium, which may be detrimental to a number of species. The use of redox mediator species like nickel hexacyanoferrate (NiHCF) can help mitigate the negative effects of the alkaline environment. NiHCF has been widely reported to serve as a redox mediator; nevertheless, most NiHCF has been synthesized using electrodeposition

on a nickel-containing solution or a nickel-metal surface, or by some other chemical process^{101,131-133}.

Oliveira *et al.* developed a quick and easy voltametric method for determining rifampicin by using a glassy carbon electrode coated with NiNPs and hexacyanoferrate¹³⁴. An unconventional approach to NiHCF electrosynthesis was used to fabricate the sensor by depositing NiNPs on the surface of several electrodes in a potentiodynamic environment. NiNPs synthesized in this process has average mean size of 40 nm and of irregular shape. [write down the role of NiNPs in this sensor with suitable figure]

3.7. Use of NiNPs for separation in the petroleum industry as magnetic nanoparticles:

Magnetic nanoparticles have many potential uses as a result of their adaptability, including those in biomedicine, environmental separation, catalysis, data storage and other disciplines¹³⁵⁻¹³⁹. It is also important to note that the added coating will alter the nanoparticle size and affect some features, such as the magnetic response of NPs containing a magnetic core. The majority of research into the application of nanotechnology to the petroleum industry has focused on the potential of functionalized NPs for reservoir mapping and magnetic nanofluids for use in drilling, completion, and increased oil recovery. Paraffin wax is a potentially problematic deposit that can form in the production tubes of petroleum processing facilities. To facilitate the melting of the wax layers, Hainande *et al.* produced NiNPs in conjunction with specially designed polymers¹⁴⁰.

3.8. Free radical scavenging and antibacterial activity of NiNPs :

Sudhasree *et al.* synthesized NiNPs through green and chemical route using polyethylene glycol and hydrazine hydrate as stabilizing and

reducing agent respectively for chemical route whereas, *Desmodium gangeticum* aqueous root extract used as precursor without any stabilizing and reducing agent for green route⁹⁹. In comparison to chemically synthesized NiNP, green-synthesized NiNPs had smaller average particle size and higher monodispersity, as seen in their study. NiNPs produced through the green approach have been shown to have superior antioxidant and antibacterial properties based on their ability to scavenge free radicals¹⁴¹.

4. Conclusions and future recommendations

In this review, numerous NiNPs synthesis approaches are categorized as either top-down or bottom-up techniques. Also mentioned physical, chemical, and biological approaches for the synthesis of NiNPs. Physical techniques of generating NiNPs are detailed, including mechanical milling, pulsed electric spark discharge, the arc-discharge method, and the pulse laser ablation approach. This process produces controlled shape and size product. The product found by this process has controlled shape and size and they are suitable for large scale production. Chemical reduction, electrochemistry, thermal breakdown, microwaves, sonochemistry, microemulsions, *etc.* have all been reported as chemical routes of synthesizing NiNPs. Low cost production makes it suitable for a wide range of production. The function and mechanisms of plant extract, bacteria, fungi, algae, *etc.* biological approaches are described. Plant extracts have become increasingly popular for their low cost, easy availability, and compatibility of most plants. Literature-reported reaction pathways for the synthesis of NiNPs from plant extracts and physical methods are discussed, along with the functional groups involved in the reduction of Ni to NiNPs. There has also been discussion regarding the applications of NiNPs in a variety of sectors, such as catalysis, biomedical applications, dye removal from industrial wastewater, the manufacture

of dye-sensitized solar cells and sensors, as electrochemical sensors, as magnetic nanoparticles and separators in the petrochemical industry, as free radical scavenging and antibacterial agent, and as high compressive strength material. The synthesis, characterisation, and potential uses of NiNPs have been the subject of a great deal of published study. Research into nickel nanoparticles in the future is anticipated to be significant because of the wide range of applications that have been proposed for this material in areas such as catalysis, energy storage, and electronics. However, the benefits of employing NiNPs as a catalyst have been emphasized, the drawbacks have not been detailed. In spite of this, there have been no conclusive studies conducted on the biological impacts of NiNPs on human, animal, or plant life. The reaction processes that have been documented in the scientific literature are inconclusive; hence, it is necessary to investigate the mechanisms that contribute to the formation of NiNPs, particularly in plant-mediated synthesis.

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