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Review Article

A review on plant extract mediated biogenic synthesis of CdO nanoparticles and their recent applications

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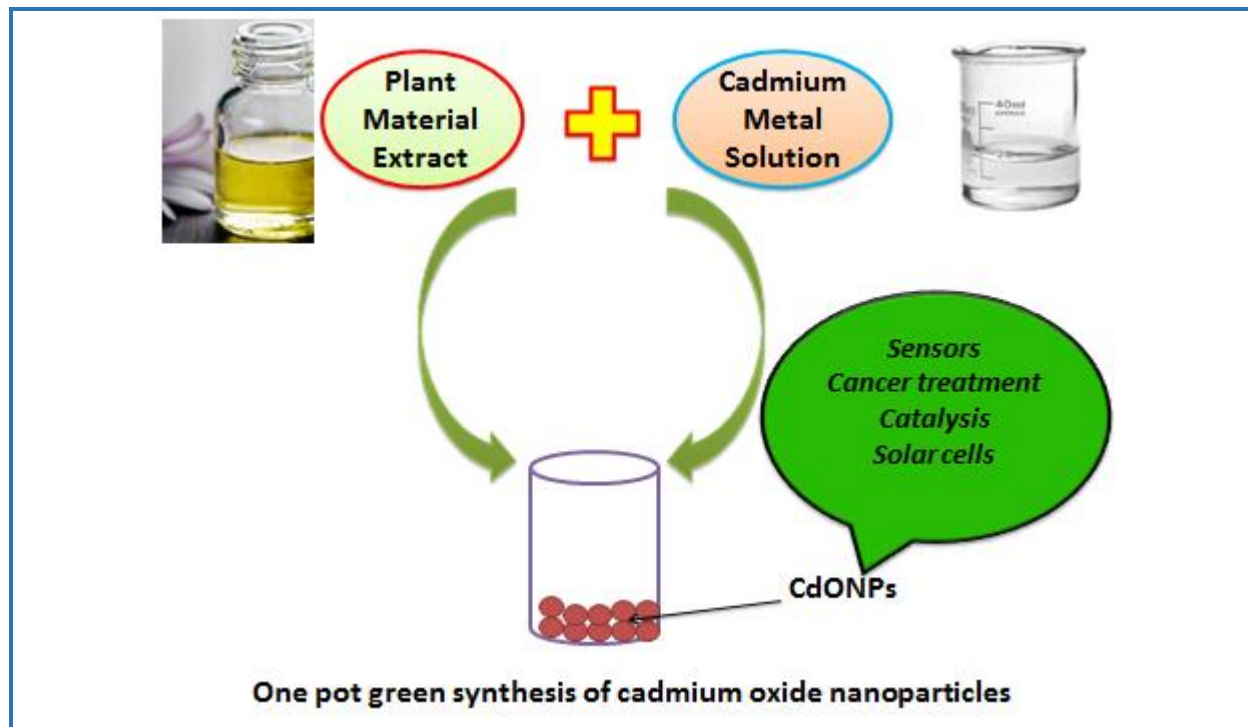
Plant extracts

CdONPs

ABSTRACT

Development of an environmentally benign route for synthesis of nanomaterial is a remarkable step in the field of nanotechnology. Nanotechnology involves the tailoring of materials at the atomic level to attain peculiar and special properties, which can be seemly manipulated for many applications. Among the all metal oxide nanoparticles, cadmium oxide nanoparticles (CdONPs) have attracted a great deal of attention due to its superior biological, chemical, and physical properties. Green protocol of synthesizing nanoparticles has emerged as an optional way to overcome the limitation of the conventional methods. Plant, biopolymers, and microorganisms are majorly used for green synthesis of nanoparticles. Using plants towards synthesis of nanoparticles are emerging and also beneficial compared to microbes with the presence of broad variability of biomolecules in plants which can act as capping and stabilizing agents and so increases the rate of stabilization of synthesized nanoparticles. Also, the nanoparticles produced by the plants material are more stable than the microorganisms. Therefore, among the all organisms plants are best potential candidates for biosynthesis of CdONPs and they are suitable for large-scale biosynthesis. In this review, the green synthesis of CdONPs, protocol of syntheses, mechanism of formation, and their miscellaneous applications have been discussed.

Graphical Abstract



Biographies



Suresh Ghotekar currently, he works as an assistant professor in the Department of Applied Science and Humanities at G. M. Vedak Institute of Technology, Tala 402 111 (Raigad) which is affiliated by University of Mumbai, Maharashtra, India. He does research in Catalysis, Synthesis of Nanomaterial and Biological Activities.

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Introduction

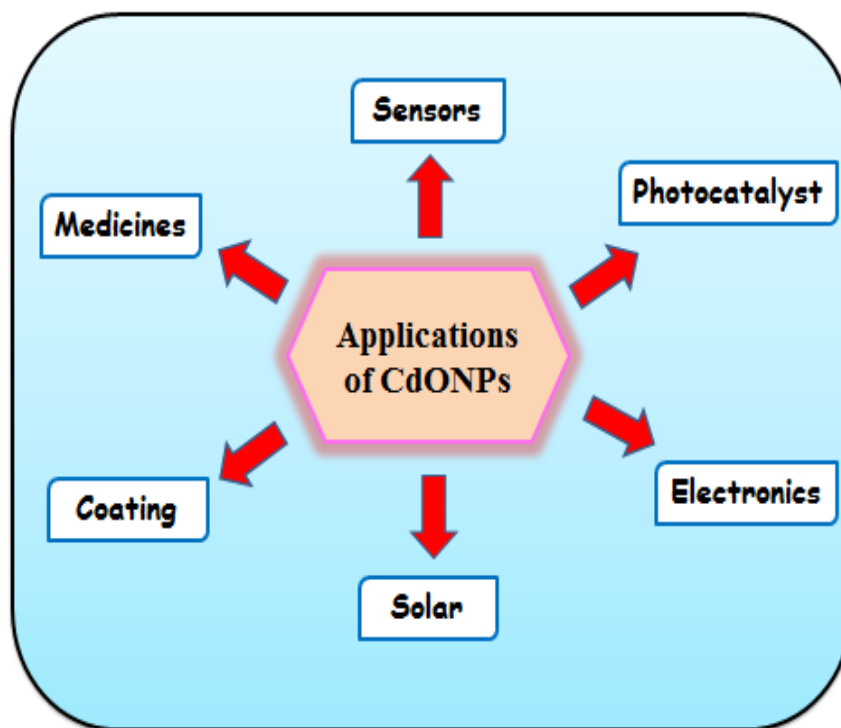
Nowadays, nanotechnology is emerging as a modern field of research, dealing with synthesis of nanomaterials for their fascinating applications in various fields including, biomedicines, catalysis, cosmetics, electrochemistry, energy science, electronics, food technology, health care, mechanics, optics and optical devices, pharmaceuticals, sensors, space industry, and textile industry [1–13]. Over the last few decades, continuous release of cadmium from various industries has created a threat to environment and human health due to its toxicity, long retention time in higher organisms, and accumulation along food chains [14]. However, CdO is a known n-type semiconductor, piezoelectric characteristics and polycrystalline in nature [15, 16]. Hence, the CdONPs are widely used specially in many applications (Figure 1) including, photodiodes, photovoltaic cells, solar cells, transparent electrodes, liquid crystal displays, IR detectors, gas sensors, and anti-reflection coating [17–20]. Therewithal, CdONPs have antibacterial, antimalarial, antituberculosis, and anticancer characteristics because of their unusual physiochemical properties [15, 16, 21, 22]. Also, CdONPs are not dangerous for human and mammalian cells at their low concentration. So, CdONPs have been widely used in a great number of industries. The action mechanism of CdONPs is similar to other metal oxide nanoparticles but its main activation is through destruction of the cell wall. This feature of CdONPs makes them very useful for eliminating cancer cells. Therefore, CdONPs have opened new horizons to scientists and researchers for the prevention of cancer and its treatment [15–23].

Hitherto, CdONPs can be easily synthesized using several methods such as chemical bath deposition [19], spray pyrolysis [24], microwave-assisted [25], photosynthetic [26], hydrothermal [27], mechanochemical milling [28], sonochemical [29], thermal evaporation [30], electrospinning [31], vapour transport [32], isothermal evaporation [33], solvothermal [34], template assisted method [35], microemulsion [36], and pulsed laser ablation [37]. Nevertheless, these synthetic routes have disadvantages like the use of drastic synthetic conditions like high temperature and pressure, long reaction time, requirement of external additives during the reaction time, need of special

instruments for experimental work and use of hazardous, toxic chemical that create biological risks and sometime these chemical processes are not simple and environmentally safe. This enhances the growing need to develop simple and environmentally friendly processes through green synthesis and other biological approaches. Some literature has been reported till to date on green synthesis of CdONPs using microorganisms including bacteria [23] and plants [15–18, 26]. Although; among the various biological methods of CdONPs synthesis, microbe mediated synthesis is not very simple and suitable for industrial feasibility because of requirements of highly aseptic conditions and their maintenance. So, the use of plant extracts for this purpose is potentially advantageous over the microorganisms due to the ease of improvement, the less biohazard and elaborate process of maintaining cell cultures [23]. It is one of the best platforms for synthesis of nanoparticles as it is free from toxic chemicals as well as providing natural capping agents for the stabilization of CdONPs. Currently, plant mediated synthesis of metal oxide nanoparticles is receiving lots of attention due to its simplicity, speedy synthesis of nanoparticles of attractive and diverse morphologies and elimination of detailed maintenance of cell cultures.

This study draws attention to the current knowledge regarding the potential of plant materials for biogenic synthesis of CdONPs and presents a database that future researchers can be based on the green synthesis of CdONPs using plants sources.

Figure 1. Applications of CdONPs



Green synthesis of CdO nanoparticles

Currently, green synthesis of nanoparticles has been an emerging research area in the field of nanobiotechnology. The advancement of green syntheses (Figure 2) over chemical and physical methods is: environmental friendly, cost effective, rapid, facile and easily scaled up for large scale syntheses of nanoparticles, furthermore there is no need to use high temperature, energy, pressure and toxic chemicals [38–40]. The use of plant material for the production of CdONPs has received lots of attention due to its simple, rapid, eco-friendly, non-pathogenic, economical protocol and providing a single step technique for the green synthesis processes [15–18]. The stabilization of CdONPs by combination of biomolecules such as tannins, coumarins, saponins, flavonoids, phenols, steroids, amino acids, carbohydrates, monoterpenoids, triterpenoids, and anthocyanins which are already established in the plant extracts having medicinal values and are environmental benign [15–18, 40]. A few numbers of plants are already reported to facilitate CdONPs synthesis and some of them are mentioned in this review (Table 1). The different parts of plant such as flowers, leaves, shoot, seeds, fruit and root are used to synthesis of CdONPs in various shapes and sizes by biological approaches. Flavonone and terpenoid components of leaf broth are being predicted to stabilize the formation of nanoparticles in comparison to high molecular weight proteins of fungal biomass [18–40]. The water soluble heterocyclic components are mainly responsible for stabilization of nanoparticles. Thereafter, the synthesized nanoparticles need to be characterized by using various techniques.

Protocol for biogenic synthesis of CdONPs

Green synthesis of the CdONPs is a facile, rapid, one-pot synthesis, and environment friendly. CdONPs have been synthesized using different parts of plants such as flowers, leaves, shoot, seeds, fruit, and root (Table 1). A very easy protocol is applied for their biogenic synthesis. The plant parts including, leaves, flowers, seeds, and fruits are collected from different sources and thoroughly washed with tap water as well as distilled water to remove other unwanted materials. The plant parts are either grinded or dried to form the powder or used directly to the preparation of plant extract. Therein, plant parts are chopped into small pieces or grinded to powder and boiled in different solvents (Ethanol and water) and boiled at suitable temperature to obtain extract. Various concentration of cadmium salts as metal precursor and plant extract can be used to synthesize CdONPs. Simply, plant extract is mixed with cadmium metal salt solution and the phytoconstituents are present in plant extract which are acts as a reducing as well as stabilizing agent for the synthesis of CdONPs. There is no need to add external chemical reducing agent or stabilizers. The detailed protocol of green synthesis of CdONPs by *Agathosma betulina* leaves extract is described by authors

reported in literature [18]. The synthesized CdONPs solution is further centrifuged to separate the nanoparticles at high rpm, and wash thoroughly with specific solvents.

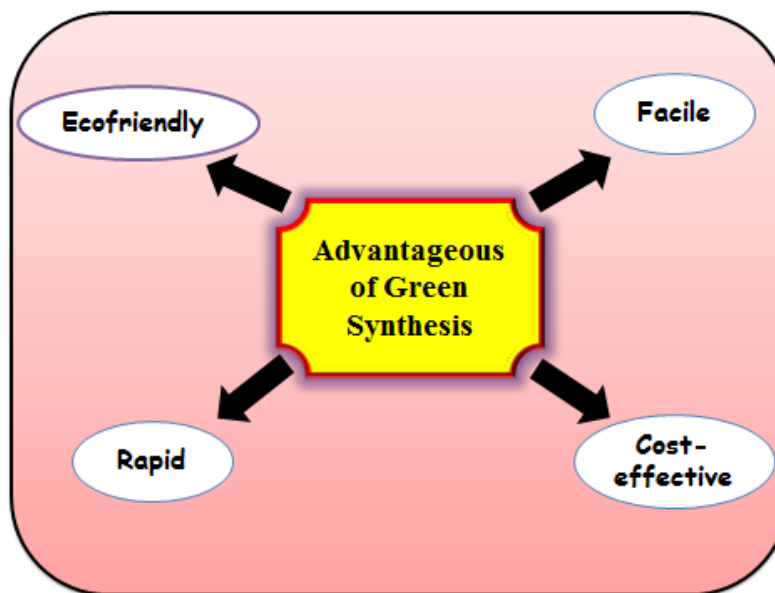


Figure 2. Importance of green synthesis of nanoparticles

Table 1. Green synthesis of CdONPs using different plant source with morphology and size

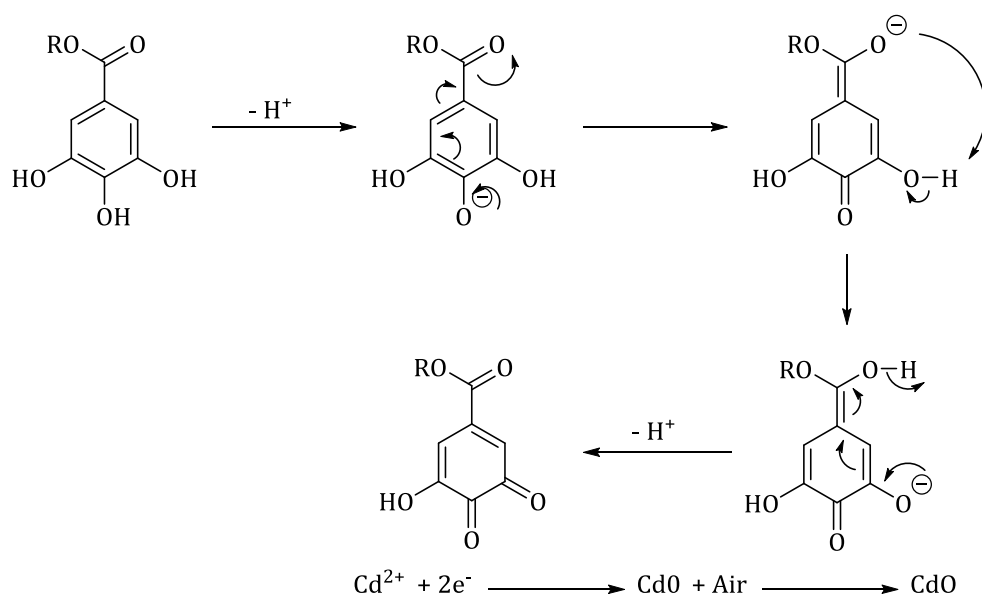
Name of Plants	Part	Precursors	Shape	Size (nm)	Ref.
<i>Achillea wilhelmssi</i>	Flowers	CdCl ₂	Spherical	35	26
<i>Convolvulus arvensis</i>	Leaves and Shoot	CdCl ₂ .2.5H ₂ O	Spherical	23 ± 2	41
<i>Agathosma betulina</i>	Leaves	Cd(NO ₃) ₂ .4H ₂ O	Quasi-Spherical	8	18
<i>Callistemon Viminalis</i>	Flowers	Cd(NO ₃) ₂ .4H ₂ O	Spherical	30–80	42
<i>Parkia speciosa Hassk</i>	Seeds	Cd(NO ₃) ₂ .4H ₂ O	Stick-like Morphology	28.92–44.95	43
<i>Hibiscus Sabdariffa</i>	Flowers	Cd(NO ₃) ₂ .4H ₂ O	Quasi-cuboidal	22.9–35	40
<i>Camellia sinensis (green tea)</i>	Leaves	CdCl ₂	Rod	41	44
<i>Andrographis paniculata</i>	Leaves	Cd(CH ₃ COO) ₂	-	22	45
<i>Leucaena leucocephala L.</i>	Leaves	Cd(NO ₃) ₂ .4H ₂ O	Spherical	36–57	15
<i>Abelmoschus esculentus</i>	Fruit	-	Spherical	18.5–89.8	46
<i>Polygala tenuifolia</i>	Root	-	Trigonal,	40–44	47

			Tetrahedron & Sheet-like Structures		
Green tea	Leaves	-	Raspberry	5–17	48

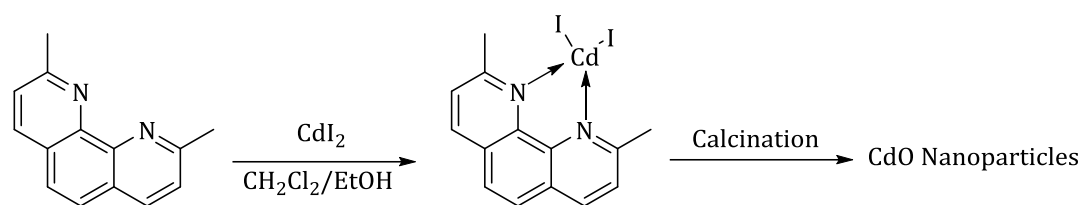
Mechanism of synthesis of CdONPs

Currently, various plant parts extract were utilized in green synthesis of metal and metal oxide nanoparticles. The biosynthesis of nanoparticles and its mechanism is dependent on phytochemicals such as tannins, coumarins, saponins, flavonoids, phenols, steroids, amino acids, carbohydrates, monoterpenoids, triterpenoids, and anthocyanins. These phytochemicals play a vital role in their synthesis using plant extracts.

Nagabhushna and co-workers synthesized CdONPs by using green tea leaves extract. He demonstrated from his studies that the polyphenol constituent like epigallocatechin gallate (EPCG) present in the extract behaves as stabilizing agent and the aromatic hydroxyl groups (Scheme 1) of EPCG adhered to cadmium ions which lead to the formation of a stable complex of cadmium and EPCG [48]. Furthermore, *Warad* and co-workers synthesized the CdONPs by using 2,9-Dimethyl-1,10-phenanthroline and CdI_2 through one step calcination process [49]. He beautifully described the mechanism of formation of CdONPs (Scheme 2).



Scheme 1. Possible mechanism of synthesis of CdONPs by using green tea leaves extract



2,9-dimethyl-1,10-phenanthroline

Scheme 2. Schematic illustration of synthesis of CdONPs

Characterization of CdO nanoparticles

Characterization is an important step to study the effect of CdONPs on environment and human health, and confirmation of their formation, different methods of their formation and monitoring their effect are required. Different characterization techniques (Figure 3) are used to characterize synthesis of CdONPs. Thermogravimetric analysis (TGA), X-ray diffraction (XRD), Scanning electron microscopy (SEM) and Transmission electron microscopy (TEM), Dynamic light scattering (DLS), Energy dispersive spectroscopy (EDS), Fourier transforms infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS), Atomic force microscopy (AFM), AFM provide surface characterization of nanoparticles at their atomic scale.

Miscellaneous applications of biogenically synthesized CdONPs

CdONPs that are synthesized via biologically green and eco-friendly route or methods provide many advantages over the synthetically manufactured one. Therewithal, on one hand these nanoparticles showed their antimicrobial activity against microorganisms, good photocatalytic property and on the other hand showed potential in drug delivery and anticancer therapy as well. I have described their remarkable applications as guidance to new researchers for future prospects (Table 2).

Herein, Khan and co-workers synthesized 23 ± 2 nm CdONPs using *Convolvulus arvensis* leaves extract and reported for the development of H_2O_2 sensor and oxidation of H_2O . They showed that the CdONPs which is a new smart material for the recognition of H_2O_2 and water splitting [41].

Balasubramanian and co-workers demonstrated the *Camellia sinensis* aqueous extract mediated CdONPs were in the size of 41 nm and showed semiconducting properties which can be utilized for electronic devices [44]. Sreekanth and co-workers described plant mediated green synthesis of CdONPs and its toxicological effects using *Polygala tenuifolia* root extract. The synthesized CdONPs are in the size of around 40–44 nm. They showed CdONPs possess significant cell growth inhibition in normal and also renal tumor cells in a dose-dependent manner [47]. Somasundaram et al.

described the biosynthesis of CdONPs using fruit extract of *Abelmoschus esculentus* and they also analyzed the antibacterial and photocatalytic activities of synthesized nanoparticles. The biogenically synthesized CdONPs were found to have spherical shape with average diameter 18.5-89.8 nm. The photocatalytic study suggests the efficiency of these biogenically synthesized nanoparticles in degrading organic dyes methylene blue under UV light irradiation. In addition, the result of antibacterial assay showed that these nanoparticles possess potent bactericidal property [46].

Figure 3. Various characterization techniques of nanomaterials

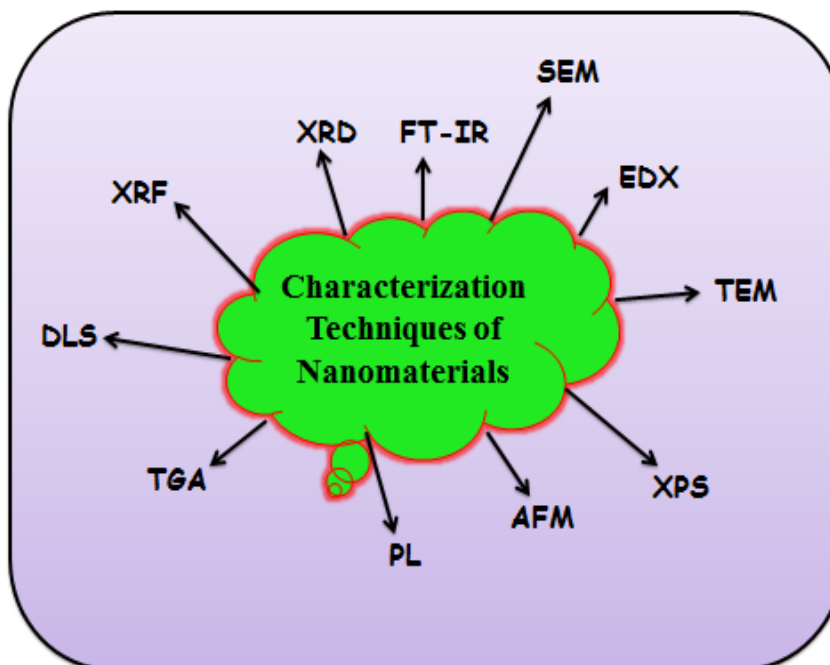


Table 2. Various applications of CdONPs fabricated using different plant extracts

Name of Plants	Applications	Ref.
<i>Leucaena leucocephala</i> L.	antimicrobial, antimalarial and antimycobacterial activities	15
<i>Hibiscus Sabdariffa</i>	solar cell	40
<i>Convolvulus arvensis</i>	H ₂ O ₂ sensing and water oxidation	41
<i>Camellia sinensis</i> (green tea)	photocatalyst and semiconducting properties	44
<i>Andrographis paniculata</i>	electrochemical and antibacterial studies	45
<i>Abelmoschus esculentus</i>	electrical, antibacterial, antifungal and photocatalytic studies	46
<i>Polygala tenuifolia</i>	Antitumor and anticancer study	47

Thereafter, *Dhanuskodi et al.* reported that the antibacterial activity of spherical CdONPs which are mediated from aqueous leaves extract of *Andrographis paniculata* [45]. Moreover, *Ghotekar* and co-workers demonstrated the *Leucaena leucocephala*, L. aqueous leaves extract mediated CdONPs were in the range of 36–57 nm and report their antimicrobial, antimalarial and antimycobacterial activity against human pathogenic bacteria [15]. From the antibacterial studies, CdONPs will be useful in the food packaging industries.

Conclusion

This review has summarized the recent research studies conducted on green synthesis of the CdONPs using few plants parts. The scrutiny of the literature surveys shows that major portion of work on biogenic synthesis of nanoparticles of gold and silver nanoparticles in comparison to CdONPs. Hence, special attention of scientific community is required to explore this eco-friendly, simple, rapid, non-toxic, and commercially viable method for synthesis of CdONPs through this biogenic bottom to top approach. Among the various biological techniques used to synthesize the CdONPs, microbe mediated synthesis is not of industrial feasibility due to the requirements of highly aseptic conditions and their maintenance. Therefore, the use of plant extracts for this purpose is potentially effective over the microorganisms due to the less biohazard, and elaborate process of maintaining cell cultures. In addition, use of plant material extracts are also reduced the cost of experiments. Therefore, green synthesis of CdONPs needs to be explored more, due to enormous availability of plant species in biodiversity. Further research should be conducted on how to use plant parts for synthesis of CdONPs.

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Abbreviations

<i>SD</i>	<i>Steam distillation</i>
<i>HAD</i>	<i>Hydro-distillation adsorption</i>
<i>SFE</i>	<i>Supercritical fluid extraction</i>
<i>DIC</i>	<i>Instantaneous controlled pressure drop process</i>
<i>MASE</i>	<i>Microwave-assisted solvent extraction</i>

<i>SCO₂</i>	<i>Supercritical carbon dioxide</i>
<i>MAE</i>	<i>Microwaves assisted extraction</i>
<i>MASD</i>	<i>Microwave-accelerated steam distillation</i>
<i>CO₂</i>	<i>Carbon dioxide</i>
<i>MILT-MHD</i>	<i>Hydro-distillation</i>
<i>CAMD</i>	<i>Compressed air microwave distillation</i>
<i>SFEM</i>	<i>Solvent-free microwave extraction</i>
<i>MHG</i>	<i>Microwave hydrodiffusion and gravity</i>
<i>VMHD</i>	<i>Vacuum microwave hydro-distillation</i>
<i>CSFME</i>	<i>Conventional solvent-free microwave extraction</i>
<i>ISFME</i>	<i>Improved solvent-free microwave extraction</i>
<i>MAHD</i>	<i>Microwave assisted hydro-distillation</i>
<i>HD</i>	<i>Hydro-distillation</i>
<i>USAE</i>	<i>Ultra-sound assisted extraction</i>
<i>%</i>	<i>Percentage</i>
<i>USWE</i>	<i>Ultrasound-enhanced subcritical water extraction</i>
<i>SLE</i>	<i>Super-heated liquid extraction</i>
<i>SE-SD</i>	<i>Solvent extraction and steam distillation</i>
<i>MSD</i>	<i>Microwave steam distillation</i>
<i>MSDF</i>	<i>Microwave steam diffusion</i>
<i>OAHD</i>	<i>Ohmic-assisted hydro-distillation</i>
<i>AFNOR</i>	<i>Association française de normalisation</i>
<i>cm</i>	<i>Centimetre</i>
<i>mm</i>	<i>Millimetre</i>
<i>°C</i>	<i>Centigrade</i>
<i>mL</i>	<i>Milliliter</i>
<i>Anhydrous MgSO₄</i>	<i>Anhydrous magnesium sulphate</i>
<i>EO</i>	<i>Essential oil</i>
<i>T_c</i>	<i>Critical temperature</i>
<i>g/cm³</i>	<i>Gram per cubic centimetre</i>
<i>α</i>	<i>This is a significant difference of 5%, which means we have a 5% chance of being wrong</i>
<i>Y</i>	<i>Yield of extrcation</i>

<i>P</i>	<i>Pressure</i>
<i>Q_{CO2}</i>	<i>Flow rate of CO₂</i>
<i>kg h⁻¹</i>	<i>Kilogram per hour conversion chart</i>
<i>Kilo Pascal</i>	<i>KPa</i>
<i>kWh</i>	<i>kilowatt hour</i>
<i>s</i>	<i>Second</i>
<i>Kg</i>	<i>Kilogram</i>
<i>CdONPs</i>	<i>Cadmium oxide nanoparticles</i>
<i>IR</i>	<i>Infra-red</i>

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