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Research Article

Green synthesis of cobalt nanoparticles by using methanol extract of plant leaf as reducing agent

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Abstract

In the present work total reducing strength or phenolic compounds in leaf extract of *Conocarpus erectus* and *Nerium indicum* were determined and then Cobalt nanoparticles (Co NPs) were synthesized by using only methanol extract of *Conocarpus erectus* leaves as reducing agent because of its higher values of total phenolic compounds (296 ± 9 µg/g) in comparison to *Nerium indicum* (185 ± 6 µg/g). Characterization of the green synthesized Co NPs was performed by SEM (Scanning Electron Microscope) and XRD (X-Ray Diffractometer) techniques. The size of Co NPs was estimated in the range of 20-60 nm. The usage of plant extract for the preparation of Co NPs makes the process cost effective, non-toxic and green method.

Key words: Co NPs; *Conocarpus erectus; Nerium indicum*

Introduction

Cobalt nanoparticles (Co NPs) show a variety of properties such as electrical, magnetic, and catalytic because of their large surface area. They also show below a critical size of 20 nm as singe-domain particles displaying quantum size effects, super para magnetism and large magnetic anisotropies **[1]**. Future applications of Co NPs in the area of catalysis, separation technology biomedicine and information storage systems, require the Co NPs to be discrete, identical in size and shape, uniform in composition and crystal structure. Several in-solution methods (liquid-phase reduction methods) are relatively simple, less expensive quicker to implement and do not require special equipment **[2]**. These methods includes; pyrolysis, microfluidic synthesis, solvo-thermal and hydrothermal decomposition, template-based methods and modified polyol processes **[3]**. Recent years Biological (or green) approach using plants or plant extracts and microorganisms for the syntheses of metal nanoparticles have recently been advised as substitutes to hazardous (chemical) methods **[4]**.

Phenolic compounds like tannins, flavonoids and phenolic acids are considered to be involved in redox activities so they are key performer to the reducing or antioxidant activity of medicinal plants, fruits or

vegetables. The phenolic compounds because of their redox activities behave as hydrogen donators, reducing agents, singlet oxygen quenchers and also metal chelating agent [5]. In plant extracts there are numerous types of phenolic compounds. They are highly reactive compounds and get involved in redox reactions. The presence of total phenolic substances within the plant extract could be liable for metal ions reduction and creation of the respective metal's nanoparticles [4].

Conocarpus erectus is the species family *Combretaceae*. It is an evergreen tree and grows on coastal areas of hot regions of the world [6]. *Nerium indicum* is also an evergreen shrub or small tree of the genus *Nerium* and family *Apocynaceae*. It also grows everywhere in tropical regions [7]. Though extract of both compounds have been reported rich in phenolic compounds but *Conocarpus* leaf extract was reported a large variety of these compounds [7, 8].

The aim of present work is to synthesize cobalt nanoparticles by using leaf extracts of plant (*Conocarpus erectus* or *Nerium indicum*) having higher values of total phenolic compounds because to the best of our knowledge through literature it was the first time to use plant leaf extract (*Conocarpus erectus* or *Nerium indicum*) for the green synthesis of Cobalt nanoparticles.

Materials and methods

All reagents such as Cobalt Nitrate and Methanol which were used throughout the research work were of analytical grade supplied by Merck (Germany) and Sigma-Aldrich (USA). Equipment were Analytical balance (Sartorius, Germany), SEM analyzer (Hitachi S4160, Japan) XRD analyzer (Karaltay, DX-2700 MIN), Magnetic stirrer/Hot plate (MS-H-Pro+), vacuum filtration assembly (Thomas 4595D45), Thermostat/incubator (Seimens), Spectrophotometer (Tomos), grinder (West point).

Preparation of extract of samples

Samples (*Conocarpus erectus* and *Nerium indicum*) were obtained from the Main Campus of NED University Karachi and they were shad-dried for one week and then they were grinded. 100 g of shade-dried leaves were grinded to form powder then it was added to 500 mL methanol, ethanol and distillated/deionized water in 1L flask and mixed vigorously. The preparation of plant extract was performed by using hot plate/magnetic stirrer at 50° C for 1 h. The acquired plant extract was filtered by vacuum filtration assembly.

Determination of total reducing strength or total phenolic compounds

Total reducing strength or total phenolic compounds in all plant extracts were determined as described by singleton *et al*. [9] with the help of spectrophotometer. Briefly 0.5 mL of extract added with 10 % Folin-Ciocalteu's reagent (2.5 mL in equal voume of 7.5 % $NaHCO_3$). Blank was prepared by adding methanol (0.5 mL), 10 % Folin-Ciocalteu's reagent (It was dissolved in water and 7.5 % $NaHCO_3$ in equal volumes of 2.5 mL). The reaction mixtures were incubated at a temperature of 45° C for 45 minutes in an incubator/thermostat. The absorbance of solution was noted at 765 nm wavelength using spectrophotometer. Standard solution of gallic acid was used as standard.

Green synthesis of cobalt nanoparticles

The cobalt nanoparticles were prepared in a 250 mL conical flask in which 50 mL cent molar solution of cobalt nitrate was mixed with 10 mL of the plant extract (100 g of dried leaves powder of was added to 500 mL methanol, ethanol and deionized/distillated water in 1L flask) along with vigorous shaking on a hot plate till the appearance of dark brown colour.

Characterization of Co NPs

The external appearance and size of produced Co NPs were characterized by using SEM

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(Scanning Electron Microscope) and X-Ray Diffractometer (XRD).

Results and discussions

Total phenolic compounds

Leaves extracts (water, ethanol and methanol) of *Conocarpus erectus* and *Nerium indicum* were investigated for total phenolic compounds and results are presented in table 1. It can be seen that the total phenolic compounds were found higher in methanol extracts (*Conocarpus erectus*, 296 ± 9 µg/g; *Nerium indicum*, 185 ± 6 µg/g) lower in water extract (*Conocarpus erectus*, 59 ± 8 µg/g; *Nerium indicum*, 27 ± 2 µg/g). As methanol leaf extract of *Conocarpus erectus* contained higher values of phenolics so in the present study it was used for the green synthesis of Co NPs.

El-Sayed *et al.* **[8]** have reported that the total phenolic compounds were higher in ethyl acetate fraction of fruits and flowers (303.45 and 301.15 mg/g GAE respectively) whereas they were lower (186.21 and 181.61 mg/g GAE) in leaves and stem. On the contrary our results shows the methanol extract of leaves contain higher values which might be due to environmental effect and choice of solvent **[10].** Vinayagam and Sudha, **[7]** has reported in scientific literature that the total reducing strength or total phenolic compounds was found to be higher in *Nerium indicum* flower extract (449 mg/100g), as compared to leaves 227mg/100g. Our selection of leaves extract as raw material for the green preparation of cobalt nanoparticles is only due to the abundance and availability of leaves throughout the year.

Table 1. Total phenolic compounds in leaves extract of *Conocarpus erectus* and *Nerium indicum*

Plant	Total Phenolic Compounds (µg/g)		
	Water	Ethanol	Methanol
Conocarpus erectus	59 ± 8	158 ± 5	296 ± 9
Nerium indicum	27 ± 2	149 ± 5	185 ± 6

Green synthesis of cobalt nanoparticles

In the present work our main focus is on the synthesis of Co NPs using reducing properties of total phenolic compounds inside the plant leaves according to the scheme/mechanism (Fig. 1). Of course, the effect of other phytochemicals inside the plant is also possible **[4].**

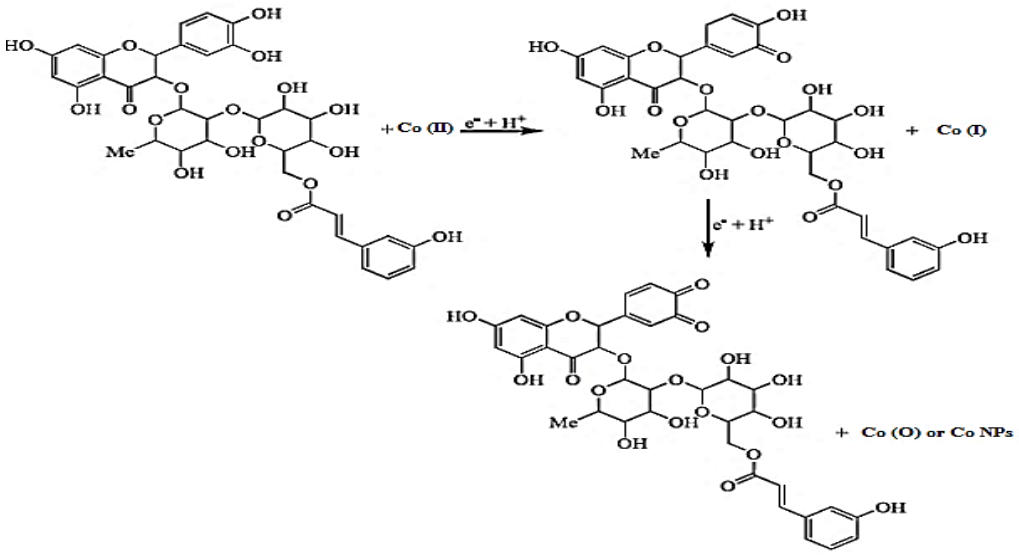

Figure 1. Scheme/Mechanism for the formation of Co NPs by phenolic compound

SEM analysis

The SEM analysis is helpful in determining the structure of the Nanoparticles (or reaction products) that were fashioned. The SEM image (Fig. 2) disclosed a number of discrete and spherical Co NPs as well as some larger groups. The SEM image of Co NPs also revealed that spherical shaped and to the some extent irregular nanoparticles were fashioned with the diameter range 20-60 nm whereas grouped particles were fashioned above the range 100 nm. Similar types of images for Co NPs were also reported by various researchers **[1- 3].**

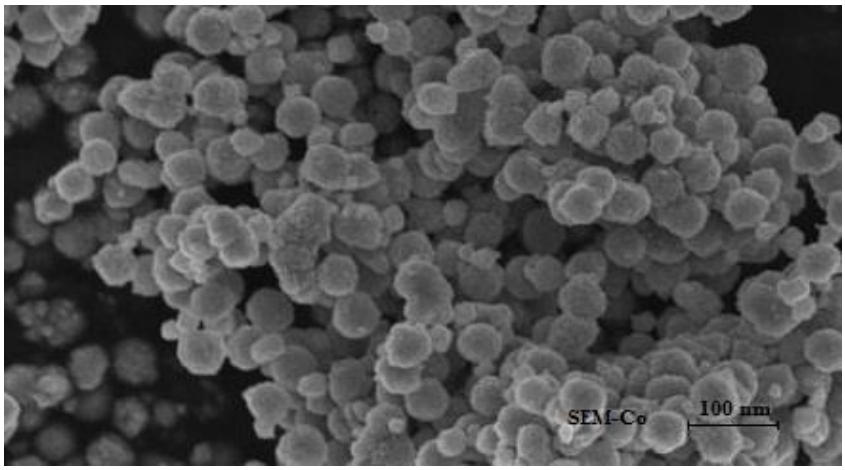

Figure 2. Scanning electron microscope image of green synthesized Co NPs by *Conocarpus erectus*

XRD analysis

The powdered sample was used for XRD Analysis in order to confirm the presence of Co NPs. Relative intensities and Peak positions [Seven peaks at 2θ values of 30, 35, 39, 43, 54, 57 and 62 degrees corresponding to (330), (311), (222), (400), (422), (511) and (440) planes of cobalt] for green synthesized Co NPs (Fig. 3) were matched to values from JCPDS (Joint Committee on Powder Diffraction Standards) card for Co file Co_HCP JCPDS #01-1278 and Co_FCC JCPDS #15-0806. The careful observations of peaks in the graph revealed that they are closed to the values with the literature report **[11]** which means exactly cobalt Nanoparticles were produced by the reaction between cobalt nitrate and methanol leaf extract of *Conocarpus erectus*

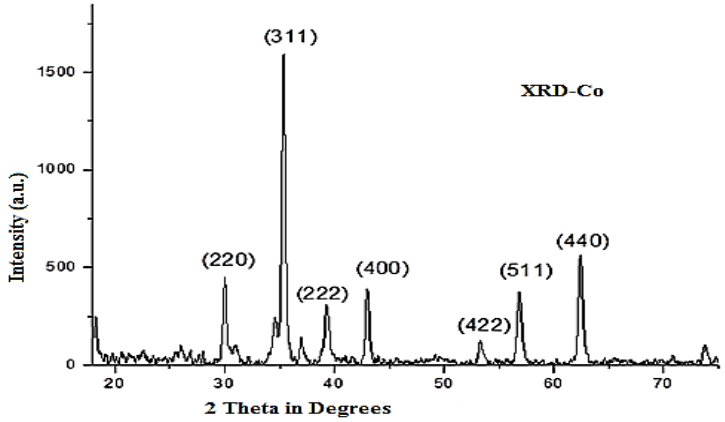

Fig. 3. XRD of Green synthesized Co NPs by leaf extract of *Conocarpus erectus*

Conclusions

It was concluded that methanol extract of *Conocarpus erectus* leaves contained higher value of total phenolic compounds (296 ± 9 µg/g) than *Nerium indicum* (185 ± 6 µg/g). It is also concluded that extract of *Conocarpus erectus* leaves can be utilized as a good reductant for the non-toxic or green synthesis of metal (Co) nanoparticles.

Authors' contributions

Conceived and designed the experiment: K Ahmed, Performed the experiment: K Ahmed, I Tariq, SU Siddiqui & M Mudassir, Analyzed the data: K Ahmed, Contributed reagent/materials/analysis tools: K Ahmed, Wrote the paper: K Ahmed

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