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Review Article

Phytochemicals Present in *Cajanus cajan* and its Use in Green Synthesis of Metal and Metal Oxide Nanoparticles

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ABSTRACT

Many attempts have been made for green synthesis of metal oxide nanoparticles; revealing the importance of plant extracts in reducing metal/ metal oxide precursor to nanoparticles and their applications in various scientific domains. *Cajanus cajan* (L.) Mill sp. (Pigeon pea), one of the pulses in human diet is legume plant, belonging to family Fabaceae or Papilionaceae. This plant has been reported to contain several phytochemicals like flavonoids glycosides, stilbenes. This article focus on applications of *Cajanus cajan* extract in fabrication of nanoparticles of various metals and metal oxides like silver, gold, titanium dioxide, zinc oxide. In respective research attempts, these nanoparticles were evaluated for one or more applications like anti-microbial activity and/or photocatalytic activity. Use of polar extract of *Cajanus cajan* indicated involvement of its polar phyto-compounds in reducing the metal source and stabilizing the nanoparticles.

Key words: *Cajanus cajan*, Phytochemicals, Nanoparticles, Anti-microbial activity, Photocatalytic activity.

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INTRODUCTION

Nanotechnology and its products are gaining vast attention of huge number of researchers due to their tremendous applications in various scientific domains. One of such wonderful nano-product is nanoparticles of metals and metal oxides. Due to wide range of utilities, several strategies have been developed for the fabrication of these nanoparticles. Increasing demand of green route of its synthesis, leads to simple way of addition of herbal extract to metal precursor solution. As this technique uses herbal extract, naturally, available phytochemicals have been found responsible for reduction of precursor to aggregation of metal ions, forming nanoparticles. These phytochemicals can be primary or secondary metabolites, which could be very specific to the plant and its organ selected for extraction. Several plants in several attempts have been found successful in reduction-based synthesis of nanoparticles of selected metal or metal oxide.[1] This review summarizes, the use of *Cajanus cajan* in green synthesis of various metal and metal oxide nanoparticles.

Cajanus cajan (L.) Mill sp. (Pigeon pea) (Figure 1), with edible seeds, is very important commercial legume crop belonging to family Fabaceae or Papilionaceae. This plant is adapted to the tropical and subtropical region and it can be grown with low fertilizer input on marginal land, even under drought condition. Genotype represents its determinate growth. It has deep tap root system which extends vertically and spread horizontally through lateral roots. Its stems are angular and woody. It has spirally arranged, pinnately trifoliate and lanceolate to oblong shaped terminal and lateral leaves, 4-17 cm in length and 3-15 mm long petiole. Due to the presence of simple or glandular hairs, leaves are pubescent. Its flowers are zygomorphic, bisexual and predominantly yellow coloured with acropetal orientation and raceme inflorescence. Pods are highly variable in size, bears 2-7 seeds.

Before exploring the uses of *C. cajan* in fabrication of nanoparticles, it will be worth noted that several phytochemicals of different classes have reported to be present in different parts of plant.

Phytochemicals present in *Cajunus cajan*

Like other plants, *Cajanus cajan* also produces several types of secondary metabolites. So far, many research reported the different phytochemicals belonging to different classes, mostly, flavonoids and stilbenes (Table 1; Figure 2). These phytochemicals may have beneficial role in *C. cajan* physiology. Here, several research articles and reviews published on isolation of any phytochemicals or phytochemical analysis of *C. cajan* have been referred.

Apart from these, terpenes mainly present in essential oils obtained from *C. cajan* leaves, seeds and stem have also been reported. These includes caryophyllene, α-calacorene, trans-nerolidol, δ-cadinene, α-selinene β-himachalene, β-bisabolene, α-Humulene allo-aromadendrene, γ-muurolene, γ-Himachalene, β-selinene, α-himachalene, longifolene, α-gurjunene, dodecanal, β-caryophyllene, β-cedrene, β-duprezianene, β-gurjunene, trans–α-bergamotene, α-guaiene, α-longipinene, cyclosativene, α-copaene, caryophyllenyl alcohol, himachalene epoxide, caryophyllene oxide etc.[12]

CAJANUS CAJAN ASSISTED SYNTHESIS OF NANOPARTICLES

So far, few research attempts were made for the synthesis of different metal and metal oxide nanoparticles using any part of *Cajanus cajan*. Usually, it involves simple addition of *C. cajan* extract to donor solution, characterisation of nanoparticles using advanced analytical techniques; and evaluation of these nanoparticles for suitable application in any

Table 1: Phytochemicals present in different parts of *C. cajan*.

Phytochemicals	Class	Reference
Leaves		
Cajanotone	Stilbenoids	2
Cajanamide A	Stilbenoids	2
Pinostrobin	Dihydroflavones	2
Naringenin 40,7-dimethyl ether	Dihydroflavones	2
Naringenin 7-methyl ether	Dihydroflavones	2
5,7-dihydroxy-8-prenylflavone	Dihydroflavones	2
Cajaninstilbene acid	Ketones	2
Amorfrutin A	Ketones	2
3-methoxy-2-(3-methylbut-2-enyl)-5-(2-phenylethyl)phenol	Ketones	2
Pinosylvin monomethyl ether	Ketones	2
Longistylin A	Ketones	2
Longistylin C	Ketones	2
Apigenin	Flavone glycosides	3
Vitexin	Flavone glycosides	4
Isovitexin	Flavone glycosides	4
Luteolin	Flavone glycosides	5
Orientin	Flavone glycosides	6
Apigenin-6,8-di-c-α-ι-arabinopyranoside	Flavone glycosides	6
Biochanin a	Isoflavone	7
Quercetin	Flavonol	3
Isorhamnetin	Flavonol	3
Cajanol	Isoflavanone	7
Pinostrobin chalcone	Chalcone	8
Cajachalcone	Chalcone	9
Cajanstilbene H	Halogen-Containing Stilbene Derivative	10
Seeds		
Quercetin-3-O-b-D-glucopyranoside	Flavonoid-O-glycosides	11
Orientin	Flavonoid-C-glycosides	11
Vitexin	Flavonoid-C-glycosides	11
Quercetin	Flavonoid aglycones	11
Luteolin	Flavonoid aglycones	11
Apigenin	Flavonoid aglycones	11
Isorhamnetin	Flavonoid aglycones	11

scientific domain. Here, research articles pertaining to synthesis of nanoparticles from any *C. cajan* extract have only been referred.

Silver nanoparticles (Ag NPs)

Silver nanoparticles have wonderful applications in various scientific domains like their antimicrobial action against various microbes, anticancer activity, photocatalytic potential etc. Understanding the significance of Ag NPs, Nagati *et al.* synthesised Ag NPs using *C. cajan* leaf extract.[13] They prepared aqueous extract of *C. cajan* leaf; added it to

Figure 1: *Cajanus cajan* plant.
1) *Cajanus cajan* plant
2) Phytochemicals present in *Cajanus cajan*: 1, cajanotone; 2, cajanamide A; 3, pinostrobin; 4, cajaninstilbene acid; 5, amorfrutin A; 6, longistylin A; 7, longistylin C; 8, cajanstilbene H.

1mM solution of silver nitrate aqueous solution and heated to 60°C for 15 min. UV-Visible spectrum showed maximum absorption at 470 nm, while FT-IR fingerprint revealed the functional groups of compounds present around the Ag NPs which includes compounds with aliphatic and aromatic amines, carboxylic acids. SEM analysis determined the size of these nanoparticles which was ranging between 5-60 nm while TEM showed that Ag NPs are spherical in shape. Further, researchers evaluated antimicrobial activity of Ag NPs against *Staphylococcus aureus* (Gram positive) and *Escherichia coli* (Gram negative) by disc diffusion assay method. The zone of inhibition exhibited by Ag Nps were found dose dependent and comparative to that with standard ampicillin.

Zinc oxide nanoparticles (ZnO NPs)

Zinc oxide is thermally and chemically stable, II–VI semiconductor having band gap of 3.37 eV. It has been studied thoroughly and used in solar cells, photo catalysts transistors, piezoelectric transducers and gas sensors.[14] Considering these applications of zinc oxide, in 2014, Manjunath *et al.* attempted to develop facile method for preparation of high quality ZnO with uniform morphologies in the form of zinc oxide nanoparticles using *C. cajan* leaves powder. They mixed zinc nitrate and pigeon pea ground powder (1:1) and stirred for 10 min in double distilled water. The system was heated to 120°C for 1 hr to get foamy mass which was then heated to 300°C to get gel. Smoldering of this gel further leads to formation of nano-crystalline ZnO. This was calcinated at 400°C for 2 hr to get ZnO NPs. Further, ZnO NPs were characterised using advanced techniques for determination of various properties, including powder X-ray diffraction (determined hexagonal zincite structure), FTIR spectral analysis (confirmed vibrational mode

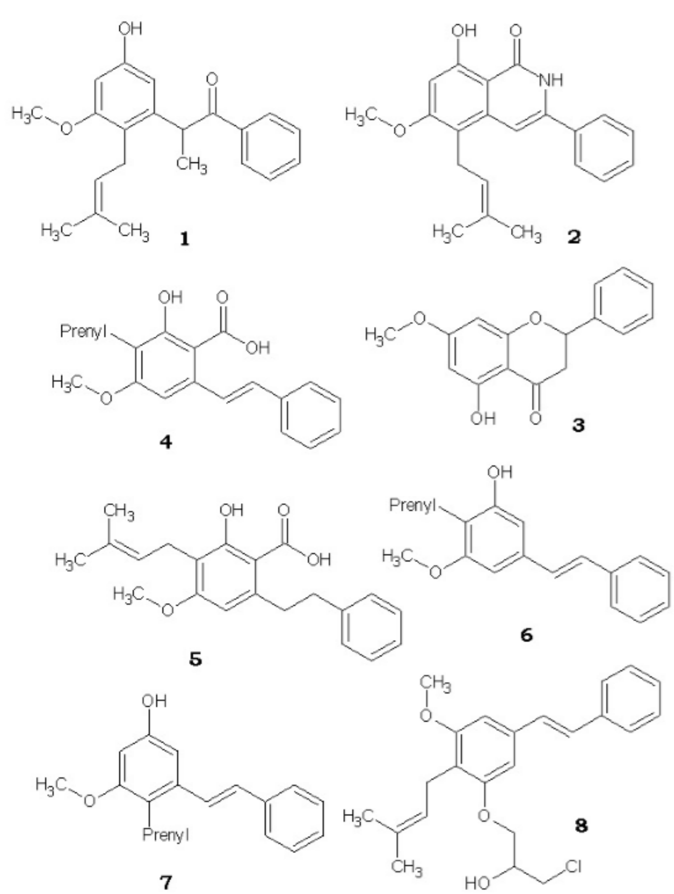

Figure 2: Phytochemicals present in *Cajanus cajan*: 1, cajanotone; 2, cajanamide A; 3, pinostrobin; 4, cajaninstilbene acid; 5, amorfrutin A; 6, longistylin A; 7, longistylin C; 8, cajanstilbene H.

of Zn-O bonding), UV-Visible spectral analysis (absorption maximum at 440 nm) and TEM analysis (determined size ranging between 40–80 nm). After characterization they determined photocatalytic activity and antimicrobial activity of so synthesized ZnO NPs. ZnO NPs assisted degradation of dye methylene blue (MB) in both sunlight and UV-light were inversely proportional to intensity of light at wavelength 665 nm. Degradation of dye was also found dye concentration and pH dependent. Higher the dye concentration, lesser is the degradation while at pH 10, degradation is highest MB is protonated. The antibacterial properties of the ZnO NPs was screened using agar well diffusion method and broth micro dilution method; against Gram negative bacteria *Klebsiella aerogenes, Escherichia coli, Pseudomonas aeruginosa* and Gram positive bacteria *Staphylococcus aureus*. During time of 24 hr, free radicals may be generated which might have interacted with bacterial cells and killed them; and thereby exhibited significant antibacterial activity, noted in terms of zone of inhibition.[15]

Titanium dioxide nanoparticles (TiO_2 NPs)

In 2019, Arif *et al*. prepared TiO_2 NPs by mixing about 90ml of 5mM titanium isopropoxide solution as a precursor with 30ml of *C. cajan* seed extract as reducing agent in the ratio of 9:3 (v/v) and stirring for 7 hr. Then, mixture was centrifuged at 9,000 rpm for 20 min to separate TiO_2 NPs which were dried at 100°C overnight and followed by calcination at 570°C in a muffle furnace for 2.5 hr. Then, they studied the interesting application of TiO_2 NPs in controlling the fouling of ultrafiltration PVDF membranes. In Bovine Serum Albumin (BSA) filtration experiment, it was observed that solutes are not deposited into the pores of TiO_2 NPs treated PVDF membranes, which indicates that the fouling process could be made physically reversible.[16]

Gold nanoparticles (Au NPs)

When gold is fabricated in nanoparticles, it has many unique properties pertaining to localized surface plasmon resonance (LSPR). The gold nanoparticles with different shapes are associated with diagnosis and therapy including cancer treatment, as anti-angiogenesis, anti-arthritic, antimalarial agents and many more. Because of their excellent photoelectrochemical and photocatalytic properties that they possesses, Au NPs are used in various devices like photovoltaic cells, photoelectrodes, optoelectronic devices sensors, photocatalysis.[17]

Due to these applications, Ananthi *et al*. 2017 explored the use of *C. cajan* leaves in fabrication of Au NPs and their evaluation of antimicrobial efficacy and anti-fouling application on metal coupons. They first prepared aqueous extract of previously sterilised fine powder of *C. cajan* leaves in Milli Q water and filtered. Then, about 10 ml of extract was mixed with 90 ml of 10^{-3} M gold chloride prepared in Milli Q water. After 24 hr, Au NPs were separated by centrifugation and characterised by advanced analytical tools. The Au NPs so synthesised were found capped with compounds having phenolic hydroxyl groups (flavonoids and/or tannins) and have absorption maximum at 540 nm. Presence of gold had been confirmed by EDS analysis while cubic shape and size (1-100 nm) were determined by SEM analysis. The ability of these green synthesized Au NPs to control the biofilm forming bacterial communities was determined by conducting the anti-microfouling studies, which indicated that Au NPs inhibit the growth and survival of biofilm forming bacteria effectively on stainless steel -SS304 metal coupons.[18]

CONCLUSION

Different parts of plant possess different classes of phytochemcials. These can be secondary metabolites like flavonoids, alkaloids, tannins, glycosides, terpenes. These types of phytochemicals are responsible for fabrication of metal and metal oxide nanoparticles. So far, silver, gold, zinc oxide and titanium dioxide nanoparticles have been synthesised using *Cajanus cajan* extracts and evaluated for different applications like photocatalytic degradation of dye and antimicrobial activity. It can be concluded that, different solvent extracts of different parts of same plant can be made and used for preparation of different nanoparticles which could further be screened for same or other applications.

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