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# Ecofriendly synthesis of silver nanoparticles using *Heterotheca subaxillaris* flower and its catalytic performance on reduction of methyl orange

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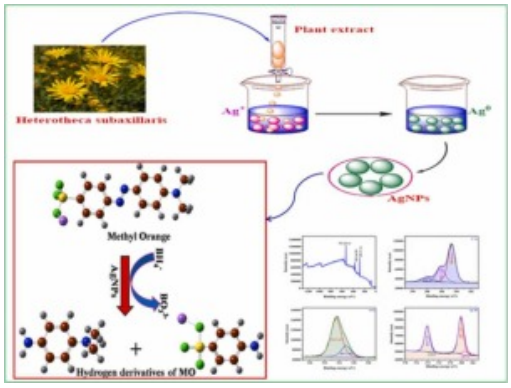
## Abstract

A green approach for the biosynthesis of silver nanoparticles (AgNPs) was developed using *Heterotheca subaxillaris* and their catalytic degradation efficiency of Methyl orange (MO) dye was explored. The formation of HS-AgNPs was monitored using UV–vis spectroscopy. The HR-TEM analysis confirmed quasi-spherical shape with the average particle size ranging from 20 to 30 nm and XRD patterns showed the face centered cubic structure. The survey scan XPS spectrum exhibited three major significant binding energy peaks at 285, 368 and 532 eV, which belong to C(1 s), Ag(3d) and O(1 s) levels of spin orbital splitting, respectively. The biosynthesized HS-AgNPs exhibited catalytic activity in the reduction of MO by $NaBH_4$, which follows pseudo first order kinetics with the rate constant of $2.1 \times 10^{-3}$ $s^{-1}$. The results prove that HS-AgNPs have an extraordinary catalytic efficiency for the degradation of MO.

## Graphical Abstract

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## Introduction

Water pollution is a major and hazardous problem in modern times. Particularly, waste effluents from the textile industry cause serious damage to the environment. The discharge of untreated dye effluents from the textile industries into water bodies affect the regular functioning of the water ecosystem, which causes serious illnesses, such as liver and kidney damages in humans. Generally, ultrafiltration, adsorption, coagulation flocculation, reverse osmosis, chlorination, ion exchange, membrane filtration, advanced oxidation processes (AOPs) and ozonation techniques have been used for the removal of organic dyes from the wastewater [1], [2], [3], [4], [5], [6], [7], [8]. However, these methods are expensive and required high maintenance. Particularly water soluble azo dyes are very persuasive in lower concentrations. They are degraded only when their azo bonds cleave leaving them into their component molecules, but it is very difficult to break the bond by simple methods [9]. Hence, it is very much necessary to develop eco-friendly and cost-effective methods for the reduction of dyes in an aqueous medium. In addition to many nonmetallic nanoparticles, there are several types of metallic nanoparticles (e.g., silver, copper, platinum, palladium, and rhodium) besides many showed greater catalytic degradation of dyes in wastewater with a short time [10]. In recent decades, it has been established that the silver nanoparticles (AgNPs) are highly active catalysts for degradation of severe organic effluents present in the wastewater [11], [12]. The AgNPs have several advantages including good biocompatibility, less toxicity and large surface-to-volume ratio as compared to the bulk material. Owing to these unique features, AgNPs are a potential candidate for the dye polluted wastewater treatment. Similarly, AgNPs have also been used for different applications including electrical conductivity [13], chemical stability [14], catalysis [15], magnetic [16], optical response [17], chemical sensors [18], biomedical applications [19], antimicrobial activity [20] and surface enhanced Raman scattering (SERS) [21] because of their inherent properties.

Generally, the metal nanoparticles are synthesized with the help of organic solvents and synthetic compounds. Utilizing synthetic compounds for developing metal nanoparticles is not desirable for the sustainable materials development. As a result, it is required to develop green synthesis method that employs eco-friendly materials (e.g., plant extracts) for the synthesis of stable nanomaterials [22]. The composition of phytochemicals like polyphenols, terpenoids [23] and biomolecules such as proteins, amino acids, vitamins, polysaccharides [24] of the plant play a vital role in the bio-synthesis of nanoparticles because they can act as both reducing as well as stabilizing agents. This study reports on the eco-friendly biogenic synthesis of AgNPs using *H. subaxillaris* flower extract as a reducing agent which reduces $Ag^{+}$ to $Ag^{0}$. It has been investigated through spectroscopic and microscopic analysis, emphasizing the catalytic efficacy. *H. subaxillaris* is commonly called as ‘camphor weed’ from *Asteraceae* family. The leaves and flowers contain characteristic strong odor of camphor from the glandules which enhance the smell of camphor. Further the camphor odor is intense due to the presence of mono and sesquiterpenoids in the flower even it provides self-defense from herbivores [25], [26]. The special qualities of these features allow to invasive succession even in dry regions. The major phytoconstituents of monoterpenes have camphor, bornyl acetate, and borneol, and major sesquiterpenes [27]. In addition to that the presence of phenolic compounds like mono and sesquiterpenoids, methylated flavonoids in the phytoconstituents plays a vital role to prevent a lot of abiotic threats and create the good ecological balance [28]. These phytoconstituents are good enough to develop allelopathic properties. This is the first report on the ability of *H. subaxillaris* flower aqueous extract used in the synthesis of AgNPs and evaluation of catalytic reduction of textile dyes.

Therefore, the aim of this study is to produce AgNPs by an eco-friendly synthetic route with *H. subaxillaris* flower aqueous extract and their usage for catalytic degradation of textile dyes with aqueous $NaBH_4$. The $Ag^{+}$ reduction to $Ag^{0}$ was observed through spectroscopic and microscopic analysis, suggesting the catalytic

efficacy. By using the general analytical methods, the biosynthesized *H. subaxillaris*–AgNPs (HS-AgNPs) are characterized systematically. The effects of synthesized AgNPs on the methyl orange (MO) dye degradation and their reaction kinetics were studied by UV–vis spectroscopy.

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## Section snippets

### Materials

*H. subaxillaris* flower occurred in open dry sandy areas and collected from Virudhunagar, Tamil Nadu, India in February 2020. The silver nitrate (purity of 99%), $NaBH_4$, and Methyl orange were purchased from Sigma Aldrich, India. All chemicals were used in these experiments without further purification due to their high degree of purity. During the entire experiment, de-ionized water was used for the preparation of *H.subaxillaris* flower extract, synthesis and preparation of solutions.…

### Preparation of *H. subaxillaris* flower extract

The dried…

### UV–vis spectroscopy

The formation of biosynthesized HS-AgNPs was monitored through UV–vis absorption spectrophotometer. The SPR absorption spectral band was observed due to the presence of metal nanoparticles on the surface based on the size and shape, which was in the form of collective oscillation of conduction band electrons with light waves [29]. The current study reported that the color of the extract was observed as pale yellow and after adding the extract to silver nitrate solution gradually it turned into…

### Conclusion

This paper demonstrates a simple, cost effective and eco-friendly synthesis of AgNPs using the flower extract of *H. subaxillaris* as reducing and stabilizing agent. The optimized HS-AgNPs exhibited the characteristic SPR band at 425 nm and remained stable for six months without agglomeration. The FTIR results revealed that the phytoconstituents present in the extract were responsible for the reduction of Ag ions to HS-AgNPs. The XRD analysis showed the face centered cubic structure of HS-AgNPs.…

### CRediT authorship contribution statement

**Rajamanickam Rajasekar**: Conceptualization, Data curation, Investigation, Visualization, Writing – original draft. **Radha Thanasamy**: Methodology, Resources, Validation. **Micheal Samuel**: Writing – review & editing. **Thomas Nesakumar Jebakumar Immanuel Edison**: Formal analysis, Software. **Natarajan Raman**: Validation, Supervision.…

### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.…

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