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Biosynthesized Silver Nanoparticles for Knoevenagel Condensation: A Comparative Study of Catalyzed and Catalyst-Free Conditions

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Abstract: *The present study explores a sustainable approach for the synthesis of silver nanoparticles (AgNPs) using Phyllanthus emblica fruit extract and their application as a heterogeneous catalyst for the Knoevenagel condensation of N-methylisatin and 5-methylisatin with rhodanine and 3-ethylrhodanine. The synthesized AgNPs exhibited characteristic nanoscale properties and good catalytic activity. The nanoparticles showed predominantly spherical morphology and a crystalline structure, while demonstrating efficient catalytic performance in aqueous conditions with good product yields. The catalyst was also recoverable and reusable, highlighting its potential as a green heterogeneous catalyst. Catalyst-free experiments under identical conditions are also important for determining the actual contribution of AgNPs to the reaction. Overall, the study demonstrates the potential of P. emblica-mediated AgNPs as a recoverable catalyst for the aqueous synthesis of isatin–rhodanine derivatives.*

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Introduction

Growing interest in sustainable methods of chemicals synthesis has led to the development of synthetic methods which would generate less waste, use fewer dangerous materials, be more efficient regarding resource use, and use safer conditions of reactions. Green chemistry allows one to consider these goals in terms of waste prevention, atom economy, safer solvents, renewable feedstocks, energy efficiency, and catalysis (Anastas & Warner, 1998; Anastas & Eghbali, 2010). Catalysis is especially relevant to green chemistry since the use of catalysts would allow performing certain chemical transformations without consuming them stoichiometrically.

One of the key factors which should be taken into account while evaluating the efficiency of chemical synthesis is atom economy. Chemical reactions in which a greater number of atoms from reactants go into the formation of a product are preferred from the point of view of resource utilization (Trost, 1991). Green parameters such as atom economy, reaction mass efficiency, process mass intensity, and the E-factor can offer more information on the sustainability of a chemical process than isolated yield (Sheldon, 2018; Jiménez-González et al., 2011).

Knoevenagel condensation is a key carbon-carbon bond forming reaction of carbonyls and active methylene reagents. Normally, Knoevenagel reaction entails the addition of an activated methylene reagent to a carbonyl compound and elimination of water resulting into the formation of an alkene-containing product. In view of its synthetic utility, the Knoevenagel condensation has been used extensively in the preparation of pharmaceuticals, heterocyclic compounds, fine chemicals, functional materials and biological molecules (Diksha & Naresh, 2022). Heterogeneous catalysis for the Knoevenagel reaction has attracted much research interest in recent years because heterogeneous catalysts offer various benefits in terms of separation, recycling, and regeneration (Appaturi et al., 2021).

Isatin, which is also known as 1H-indole-2,3-dione, is an important heterocyclic unit in synthetic and medicinal chemistry. Its two carbonyl moieties and easily substitutable nitrogen atom allow considerable opportunities for the diversity of its structure. Isatin analogs have been extensively studied in the preparation of biologically active substances and showed diverse pharmacological activities, among which are antimicrobial, anticancer, anti-inflammatory, anticonvulsant, and antiviral effects (Pakravan et al., 2013; Varun et al., 2019; Gabr et al., 2017). Moreover, electrophilicity of its carbonyl group in the 3-position makes isatin suitable for condensation reactions.

Rhodanine, which is also called 2-thioxothiazolidin-4-one, is a sulfur- and nitrogen-containing five-membered heterocyclic compound, characterized by the presence of an activated C-5 methylene group. The acidity of such a methylene group is caused by its location between the two electron-withdrawing groups, namely, carbonyl and thiocarbonyl, and makes rhodanine an ideal candidate for the Knoevenagel condensation with carbonyl compounds. Due to the possibility of structural modifications of the ring nitrogen atom and the activated carbon atom, rhodanine analogues have drawn much attention of researchers recently as such modifications can result in a variety of biological activities (Tomasić & Mašić, 2009; Song et al., 2012; Chaurasyia et al., 2023). This issue has been discussed in the recent literature review (Lim et al., 2022; Das et al., 2025).

Nanomaterials have shown great potential as catalysts, since their small sizes ensure a high ratio of the surface area to volume and availability of numerous surface sites. The properties of metallic nanoparticles are highly dependent on their size, morphology, surface chemistry, and aggregation state (Khodashenas & Ghorbani, 2015). This makes metal nanoparticles suitable candidates for various catalytic, optical, biological, and environmental applications (Wei et al., 2015; Deshmukh et al., 2019).

Among metallic nanomaterials, silver nanoparticles have been extensively studied due to their unique optical, electronic, surface, and catalytic properties. The application areas of AgNPs range from catalysis, sensing and antimicrobial applications, to environmental applications and biomedical research (Sharma et al., 2009; Wei et al., 2015). The catalytic activity of AgNPs depends largely on the availability of surface sites, particle size and morphology, and interactions between the adsorbed species and surface of the nanoparticle.

The traditional methods of production of metal nanoparticles usually involve using chemical reducing agents, stabilizers, organic solvents, or other additives. These procedures can lead to the formation of extra waste or substances which are not environmentally friendly. Therefore, biological and plant-based techniques are gaining popularity as promising alternatives (Mohanpuria et al., 2008; Iravani, 2011; Mittal et al., 2013). Extracts of plants are quite advantageous since they possess natural metabolites able to take part in the reduction and stabilization of metal ions. Phenols, flavonoids, carbohydrates, proteins, organic acids, terpenoids, and many others can be involved in nucleation and surface stabilization of nanoparticles (Chung et al., 2016;). There are many plants that have been successfully employed in the plant-mediated synthesis of AgNPs. For instance, Geranium leaves' extract has been used to produce crystalline AgNPs through an extracellular method (Shankar et al., 2003). In the same way, there are several plants such as Ocimum sanctum, Acalypha indica, Hibiscus rosa-sinensis, and Dillenia indica that have been explored for their use in the production of silver nanoparticles (Ahmad et al., 2010; Krishnaraj et al., 2010; Philip, 2010; Singh et al., 2013).

A plant species of significance to the current research is Phyllanthus emblica L., which is commonly referred to as Amla or Indian gooseberry. The plant contains a variety of phytochemicals such as vitamin C, phenolics, tannins, flavonoids and other active compounds. These phytochemicals are responsible for the nutritional and medicinal value of the plant (Ahmad et al., 2021). Notably, Emblica officinalis fruit extract has earlier been shown to be a biological reducing agent in the synthesis of silver and gold nanoparticles (Ankamwar et al., 2005).

A few studies have proved that AgNPs synthesized using plants can serve as catalysts. Biosynthesized AgNPs have been considered to be effective in the reduction of organic contaminants, while Ag containing heterogeneous systems have also been used for carbon-carbon bond formation reactions (Sharma et al., 2015; Chouhan et al., 2017). Plant-based AgNPs have been used as catalysts for the synthesis of heterocycles, showing the scope of organic reactions along with biological nanoparticle synthesis.

Water can also be an important ingredient of sustainable reaction design. While water itself is not necessarily considered green, it offers some unique advantages such as lower dependency on volatile organic solvents, easy handling, and reaction behavior in certain cases (Simon & Li, 2012; Cortes-Clerget et al., 2021). Thus, water-mediated organic synthesis has emerged as an important field of sustainable chemistry.

At the same time, the catalytic nature of a synthetic process must be demonstrated carefully. A reaction that gives a high yield in the presence of a catalyst does not necessarily establish that the catalyst is responsible for the transformation. Some organic reactions, including condensations involving highly activated substrates, may occur under catalyst-free conditions. Consequently, appropriate blank reactions are necessary to distinguish intrinsic substrate reactivity from catalytic acceleration (Gawande et al., 2013). This issue is particularly relevant to Knoevenagel condensation because the active methylene component can possess sufficient acidity to participate in the transformation without an externally added catalyst.

In the present investigation, *P. emblica* fruit extract was employed for the biosynthesis of AgNPs, and the resulting nanoparticles were evaluated as a heterogeneous catalyst for the Knoevenagel condensation of N-methylisatin and 5-methylisatin with rhodanine and 3-ethylrhodanine. The principal objective was to examine the performance of the biosynthesized nanoparticles under different solvent conditions and identify an appropriate reaction medium. In addition, a catalyst-free control framework is incorporated to provide a scientifically rigorous basis for determining the actual contribution of the AgNP catalyst.

Materials and Methods

- **Materials**

The Isatin derivatives, rhodanine, 3-ethylrhodanine, silver sulphate (Ag2SO4), methanol, ethanol, acetone, ethyl acetate, and other analytical grade chemicals were used as such unless stated otherwise. Thin layer chromatography was monitored using silica gel plates. Distilled water was used for all aqueous reactions.

Fruits of Phyllanthus emblica were chosen as the plant source to prepare the methanolic extract.

- **Preparation of *Phyllanthus emblica* Fruit Extract**

The preparation of plant material was done by drying and then grinding it prior to extracting it. Ten grams of ground plant material from P. emblica fruit was added into a 250 mL round bottom flask together with 30 mL methanol. The two were allowed to undergo refluxing for 48 hours to aid in the extraction process of phytochemical compounds. The extracted solution was isolated through distillation process.

The utilization of plant material for nanoparticle synthesis can be compared with previous biological processes where metabolites from plants play a vital role in reduction and stabilization of metal nanoparticles (Mittal et al., 2013; Thomas et al., 2024).

- **Green Synthesis of Silver Nanoparticles**

To synthesize the AgNP, 0.5 ml of methanolic fruit extract of P. emblica was mixed with 20 ml of 0.1 M Ag_2SO_4 aqueous solution. The reaction mixture was kept under stirring and room temperature conditions. The reaction resulted in a gradual colour change from pale yellow to dark brown, which indicated the formation of AgNPs. The synthesis of AgNPs was characterized with the help of UV-visible spectrophotometry for seven days. Spectra were taken in the wavelength range between 300 and 700 nm. Formation of plant-derived AgNPs often results in the presence of surface plasmon resonance peak due to the oscillation of conduction electrons present in the nanoparticles (Sharma et al., 2009 and Khodashenas).

- **Characterization of AgNPs**

The synthesized nanoparticles were characterized using UV–visible spectroscopy, SEM, TEM, HRTEM, SAED, and XRD.

UV–visible spectroscopy was used to monitor the characteristic SPR absorption. SEM was employed to examine particle morphology and aggregation, whereas TEM was used to determine particle size and shape. XRD was employed to determine the crystalline phase and estimate crystallite size using the Debye–Scherrer equation.

The combined use of UV–visible spectroscopy, electron microscopy, and XRD is widely employed for evaluating plant-mediated AgNPs (Poudel et al., 2022; Zulfiqar et al., 2024).

- **General Procedure for AgNP-Catalyzed Knoevenagel Condensation**

N-Methylisatin or 5-methylisatin (1 mmol) was reacted with rhodanine or 3-ethylrhodanine (1 mmol) in 10 mL of the selected solvent. For catalytic reactions, 20 mg of the dried biosynthesized AgNPs was added to the reaction mixture. The mixture was refluxed and reaction progress was monitored periodically by TLC.

Water, ethanol, acetone, and ethyl acetate were investigated as reaction media. After completion of the reaction, the mixture was cooled and the product was isolated.

- **Catalyst-Free Control Reactions**

To evaluate the contribution of AgNPs to the Knoevenagel condensation, control reactions were performed in the absence of the catalyst while maintaining the same reaction conditions. In these experiments, 1 mmol of the respective isatin derivative and 1 mmol of rhodanine or 3-ethylrhodanine are refluxed in 10 mL of the selected solvent without adding AgNPs. The reaction progress was monitored using the same TLC procedure employed for the AgNP-catalyzed reactions.

The reaction time and isolated yield obtained under catalyst-free conditions is compared with those of the corresponding AgNP-catalyzed reactions. This comparison helped to determine the extent to which the observed reaction efficiency is attributable to the presence of AgNPs.

- **Catalyst Recovery**

Following completion of the catalytic reaction, the AgNP catalyst was separated from the reaction mixture by centrifugation. The recovered nanoparticles were washed with ethanol and distilled water, dried, and subsequently used in further reactions.

Results and Discussion

- **Formation of Silver Nanoparticles**

The formation of AgNPs was initially indicated by the transformation of the reaction mixture from pale yellow to dark brown (Figure 1). The colour change is associated with the optical response of nanoscale metallic silver and is commonly observed during plant-mediated AgNP synthesis.

The use of plant extracts as reducing and stabilizing agents has been widely reported. The natural phytochemicals could help reduce the Ag^{+} ions while also binding to the surface of the nanoparticles and restricting their aggregation. This technique is particularly pertinent to this experiment since it has already been shown that P. emblica can help form silver nanoparticles.

Figure 1: Formation of AgNPs

- **UV–Visible Spectroscopic Analysis**

The synthesized AgNPs exhibited a distinct absorption band at approximately 426 nm. The appearance of an SPR band in this region supports the formation of nanoscale metallic silver (Figure 2).

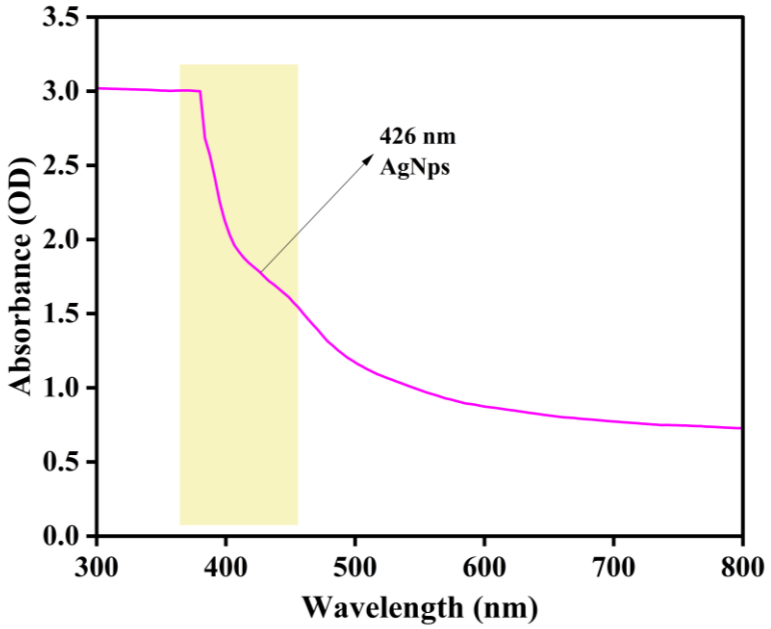


Figure 2: UV- Vis spectra of AgNPs

- **SEM Analysis**

The morphology and distribution pattern of the synthesized silver nanoparticles (AgNPs) was examined using scanning electron microscope (SEM). The results obtained through SEM observations showed that the nanoparticles have predominantly quasi-spherical shapes with uniform distribution. Most of the nanoparticles were found to be well dispersed, although some aggregation was also observed. This aggregation might be due to the phytoconstituent present in Phyllanthus emblica that can react with the surface of the nanoparticles and act as capping/stabilizing agents for AgNPs (Huang et.al., 2007). Through SEM, it has been estimated that the size of the nanoparticles is 20–40 nm(Figure 3).

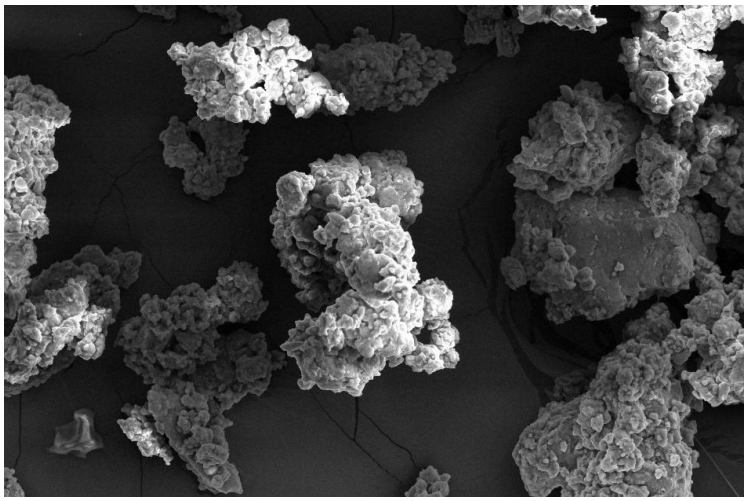


Figure 3: Sem analysis of AgNPs

- **TEM and HRTEM Analysis**

Transmission Electron Microscopy (TEM) was used for studying the morphology and particle size distribution of the AgNPs prepared via the biosynthesis process. From the TEM images, it was clear that the nanoparticles were primarily spherical or quasi-spherical in shape with particle size of about 15-25 nm (Figure 5). A coating layer of organic material was found to be present around the particles indicating the role of phytoconstituents of the P. emblica extract as capping and stabilizing agents, especially polyphenols (Bar et al., 2009).

The HRTEM studies showed clear lattice fringe patterns with a spacing of 0.235 nm. This value corresponds to the (111) plane of the face centered cubic structure of silver metal. Moreover, the selected area electron diffraction (SAED) showed the ring patterns with (111), (200), (220), and (311) crystal planes (Figure 4).

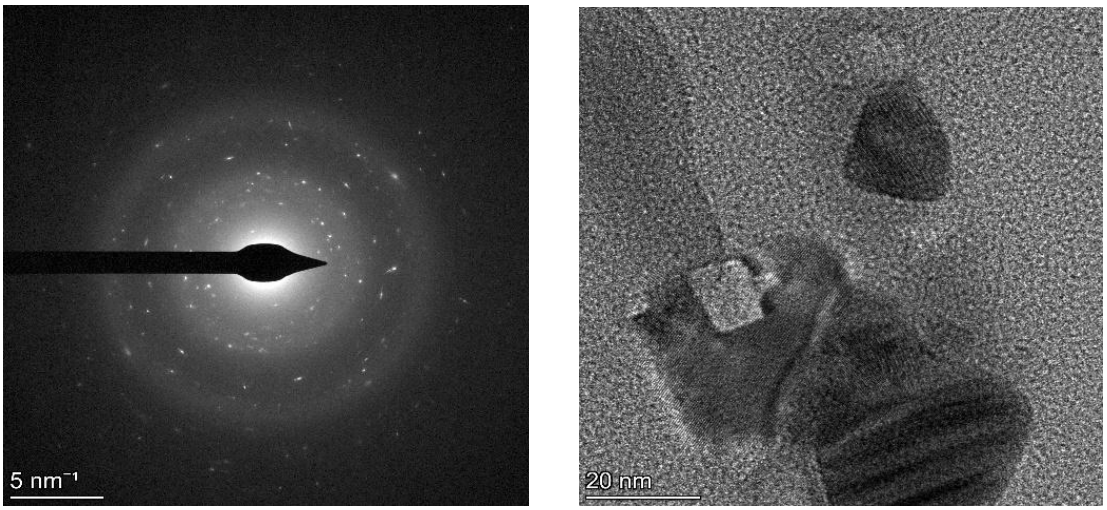


Figure 4: TEM of AgNPs

- **XRD Analysis**

The crystal structure of the prepared AgNPs was analyzed using the technique of x-ray diffraction (XRD). The obtained XRD pattern displayed sharp diffraction peaks at 2θ positions 38.1°, 44.3°, 64.4°, and 77.5°. These diffraction peaks correspond to the planes of (111), (200), (220), and (311), respectively, which are indicative of the face-centered cubic (fcc) structure of metal silver. The obtained diffraction peaks matched well with the standard JCPDS card of silver (Card No. 04-0783). The high intensity of the (111) diffraction peak suggests that the AgNPs preferentially orient on this plane.

The mean crystallite size of the synthesized AgNPs was calculated from the broadening of the XRD reflections using the Debye–Scherrer equation:

$$D = K\lambda/\beta \cos \theta$$

where D represents the average crystallite size, K is the Scherrer constant, λ denotes the wavelength of the X-ray radiation, β is the full width at half maximum (FWHM) of the selected diffraction peak, and θ is the corresponding Bragg angle (Figure 5).

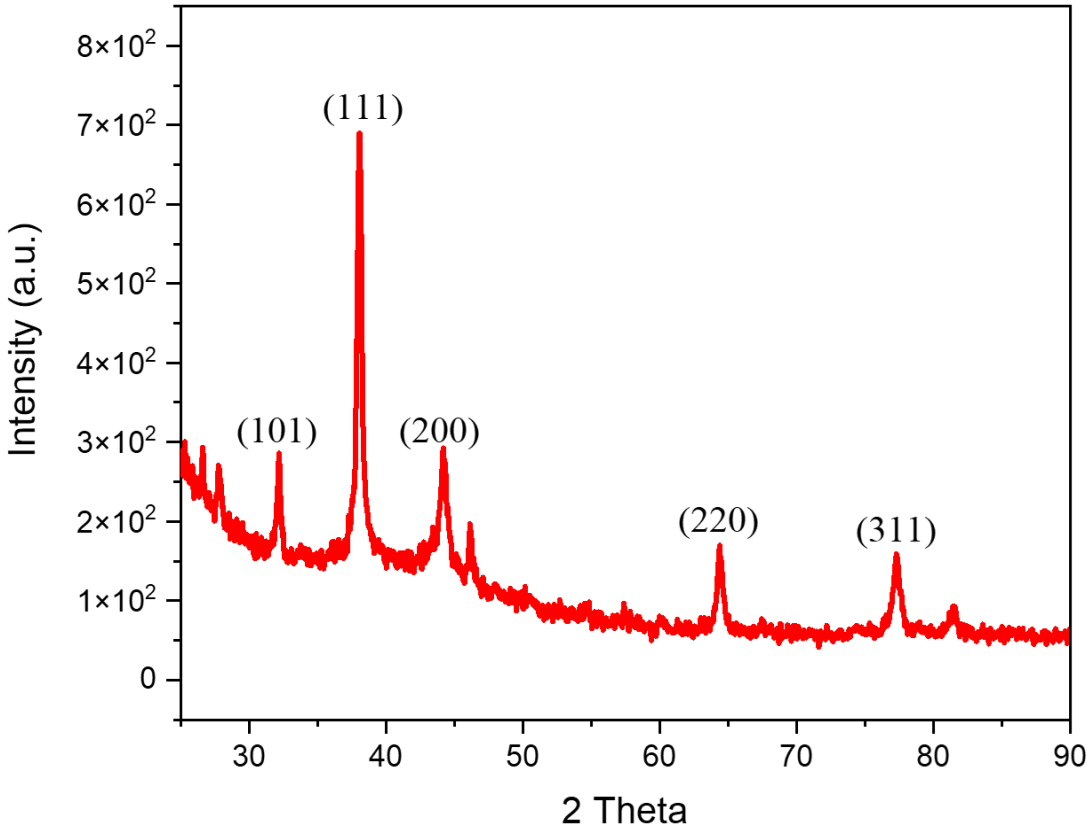


Figure 5: XRD of AgNPs

Table 1 describes the physicochemical aspects of Green synthesized silver nanoparticles

Table 1: Physicochemical characteristics of the biosynthesized AgNPs

Characterization technique	Major observation	Characteristic feature
UV–Visible spectroscopy	Distinct SPR absorption	~426 nm
SEM	Spherical/quasi-spherical particles with mild aggregation	20–40 nm
TEM	Predominantly spherical particles	15–25 nm
HRTEM	Well-defined lattice fringes	d ≈ 0.235 nm, (111)
SAED	Crystalline diffraction rings	(111), (200), (220), (311)
XRD	Characteristic silver reflections	fcc Ag; crystallite size ≈21.3 nm

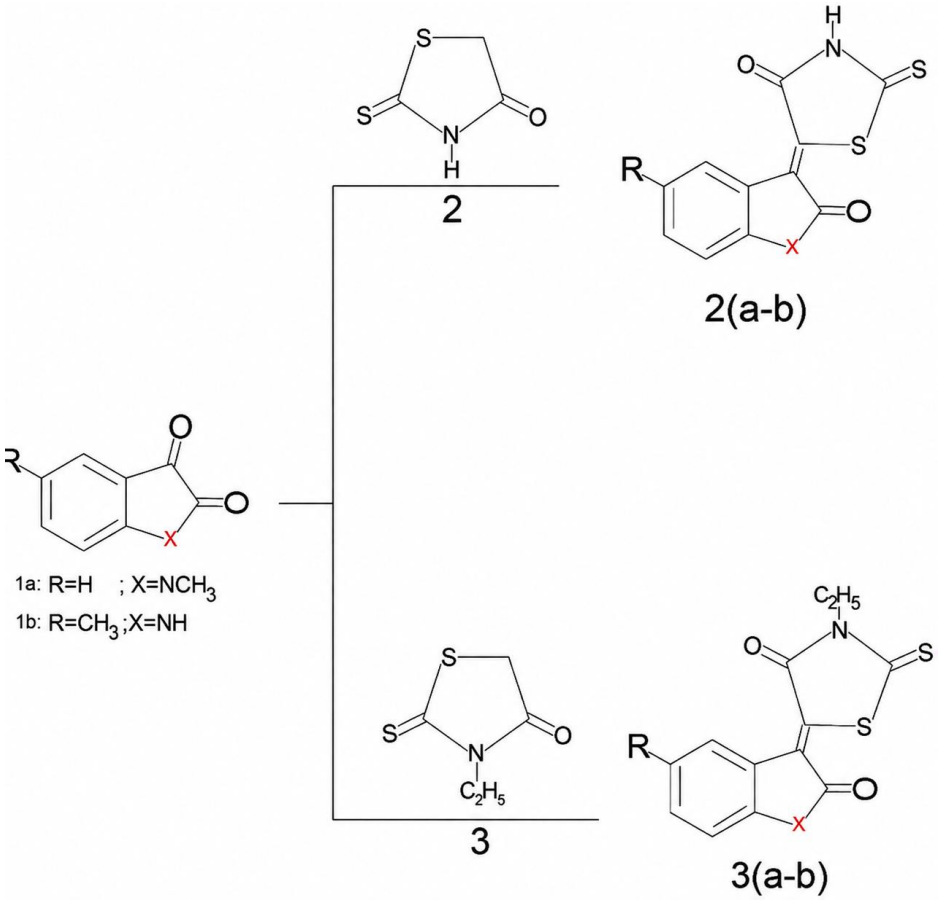
The combination of UV–visible, SEM, TEM, HRTEM, SAED, and XRD therefore provides complementary evidence supporting the formation of crystalline silver nanoparticles.

Catalytic Knoevenagel Condensation

- **Reaction Design**

The catalytic transformation investigated in this study involved condensation between the carbonyl group of N-methylisatin or 5-methylisatin and the activated methylene group of rhodanine or 3-ethylrhodanine.

The general transformation can be represented in Scheme 1



Scheme 1: The Knoevenagel type condensation reaction of N-Methylisatin and 5-Methylisatin with active methylene heterocycles viz rhodanine and N-ethyl rhodanine

The high acidity of the C-5 methylene group of rhodanine is associated with stabilization of the resulting nucleophilic species by the neighboring electron-withdrawing carbonyl and thiocarbonyl groups. Consequently, rhodanine and its N-substituted derivatives are widely used in Knoevenagel chemistry.

- **Solvent Optimization**

The catalytic reactions were investigated in water, ethanol, acetone, and ethyl acetate. The objective was to determine a suitable reaction medium for the AgNP-catalyzed condensation and summarized in Table 2.

Table 2: Effect of solvent on AgNP-catalyzed Knoevenagel condensation

No.	Isatin derivative	Active Methylene Compound	Solvent	Time	Yield
1	N-Methylisatin	Rhodanine	Water	1.5 h	82%
2	N-Methylisatin	Rhodanine	Ethanol	2.8 h	70%
3	N-Methylisatin	Rhodanine	Acetone	3.5 h	62%
4	N-Methylisatin	Rhodanine	Ethyl acetate	3.8 h	58%
5	N-Methylisatin	3-Ethylrhodanine	Water	1.4 h	84%
6	N-Methylisatin	3-Ethylrhodanine	Ethanol	2.6 h	72%
7	N-Methylisatin	3-Ethylrhodanine	Acetone	3.3 h	65%
8	N-Methylisatin	3-Ethylrhodanine	Ethyl acetate	3.6 h	60%
9	5-Methylisatin	Rhodanine	Water	1.6 h	80%

10	5-Methylisatin	Rhodanine	Ethanol	2.9 h	68%
11	5-Methylisatin	Rhodanine	Acetone	3.6 h	60%
12	5-Methylisatin	Rhodanine	Ethyl acetate	3.9 h	56%
13	5-Methylisatin	3-Ethylrhodanine	Water	1.5 h	83%
14	5-Methylisatin	3-Ethylrhodanine	Ethanol	2.7 h	71%
15	5-Methylisatin	3-Ethylrhodanine	Acetone	3.4 h	63%
16	5-Methylisatin	3-Ethylrhodanine	Ethyl acetate	3.7 h	59%

The results clearly indicate that water provided the most favourable reaction medium among the solvents investigated. In all four substrate combinations, the aqueous reactions gave the highest yields and shortest reaction times.

For N-methylisatin with rhodanine, the yield increased from 58% in ethyl acetate to 82% in water, while the reaction time decreased from 3.8 to 1.5 h. Similarly, N-methylisatin with 3-ethylrhodanine afforded 84% yield in water compared with 60% in ethyl acetate.

The same trend was observed for 5-methylisatin. The reaction with rhodanine gave 80% yield in water compared with 56% in ethyl acetate, whereas the reaction with 3-ethylrhodanine provided 83% in water compared with 59% in ethyl acetate.

The improved behaviour in water may arise from a combination of solvent effects, reactant–catalyst interactions, nanoparticle dispersion, and the physical properties of the reaction system. Water can also influence organic reactions through hydrogen bonding, hydrophobic interactions, and interfacial effects.

From a green chemistry perspective, the preference for water is advantageous because it reduces the reliance on conventional volatile organic reaction media.

Comparison of Catalyzed and Catalyst-Free Reactions

- **Importance of the Catalyst-Free Control**

An essential issue in heterogeneous catalytic research is the difference between catalytic promotion and spontaneous or thermal promotion of the reaction.

The fact that the reaction goes efficiently in the presence of AgNPs means that the chosen catalytic system is suitable for the reaction. But it cannot prove the extent of catalytic activity on its own.

It is especially important for Knoevenagel condensation since active methylene compounds are acidic enough to react in condensation with certain carbonyl compounds without any catalyst. Catalyst-free reactions in aqueous media are also a well-known field of green organic synthesis.

Therefore, a proper comparison of catalytic vs. uncatalyzed reaction should involve the same amounts of substrate, volume of solvent, temperature, atmosphere and control method, differing only by the presence or absence of AgNPs.

- **Comparative Experiment**

In order to assess the effect of AgNPs on the catalytic process, comparative experiments were conducted under similar conditions in the presence of and in the absence of the catalyst. In both cases, an equal amount of substrate and the solvent system were used, but the catalyst was not present in the case of reactions without the catalyst.

Table 4: Comparison of AgNP-catalyzed and catalyst-free reactions

Substrate combination	Catalyst	Solvent	Reaction time	Yield (%)
N-Methylisatin + rhodanine	AgNPs	Water	1.5 h	82
N-Methylisatin + rhodanine	None	Water	7 h	75
N-Methylisatin + 3-ethylrhodanine	AgNPs	Water	1.4 h	84
N-Methylisatin + 3-ethylrhodanine	None	Water	8 h	72
5-Methylisatin + rhodanine	AgNPs	Water	1.6 h	80
5-Methylisatin + rhodanine	None	Water	6.5 h	74
5-Methylisatin + 3-ethylrhodanine	AgNPs	Water	1.5 h	83
5-Methylisatin + 3-ethylrhodanine	None	Water	7.5 h	78

From the comparative study, it is observed that the reactions carried out with the use of AgNPs attained completion much more quickly than the catalyst-free reactions. The time taken for completion of AgNP-catalyzed reactions was 1.4–1.6 hours, whereas the time taken by the reactions without the use of any catalyst was 6.5–8 hours. It is also observed that the yield percentage obtained using AgNPs was 80% to 84%, whereas the yield without any catalyst was 72% to 78%.

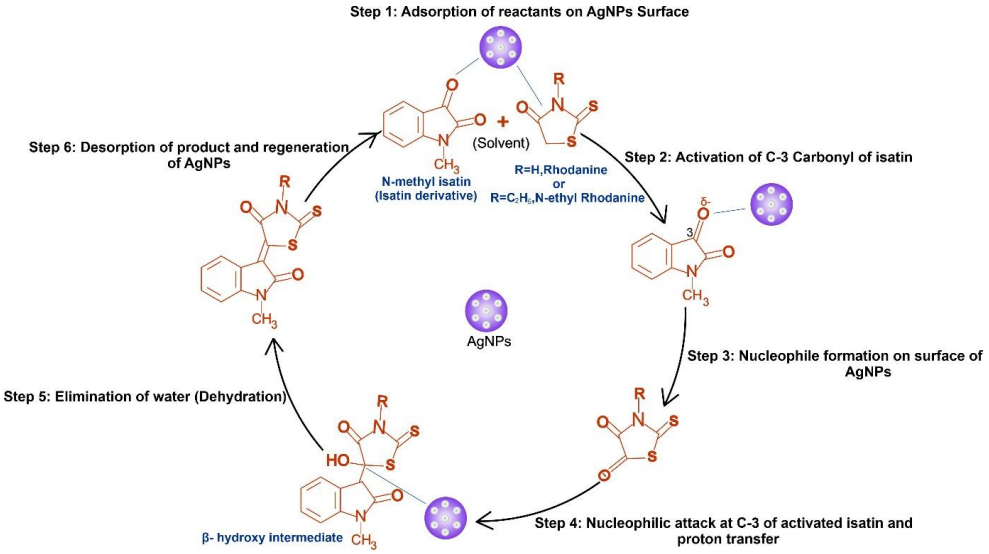
Proposed Catalytic Mechanism

One possible way that explains the Knoevenagel condensation via AgNP catalysis is given in Scheme 2. In this case, the catalyst promotes the reaction by the following steps. First of all, adsorption of both isatin derivative and active methylene compounds on the surface of biosynthesized AgNPs takes place. The high surface area of nanoparticles allows easy interaction of these compounds with active sites on the nanoparticle surface. Surface silver complexes can interact with carbonyl oxygen of the isatin derivative, which results in polarization of the C=O bond and increase in the electrophilicity of the carbonyl carbon. On the other hand, the interaction of active methylene compound with the surface allows its deprotonation.

The phytochemical molecules resulting from Phyllanthus emblica and existing on the surface of nanoparticles might also help in the stabilization of adsorbed molecules through hydrogen bonding and electrostatic interactions. The nucleophilic molecules thus formed further react with the activated carbonyl carbon of the isatin molecule to produce a β-hydroxy intermediate on the surface of the nanoparticles. Water is then eliminated from this molecule to obtain the Knoevenagel condensation molecule, having C=C bond attached to it. In the end, the products dissociate from the nanoparticle surface to provide catalytic sites again to the AgNPs.

It has not been experimentally proven what actually happens electronically and with charge transfer on the AgNP surface in this work; hence, it should be noted that the proposed mechanism of the reaction is just one of the probable interpretations rather than a real reaction mechanism. The increased efficiency of the reaction might be due to the nanoparticle's capability to activate and adsorb the reagents, stabilize reaction intermediates and transition states, and assist in forming the reactive nucleophilic species. This can result in lowering the energy barrier and increasing the speed of the condensation reaction. This surface-mediated catalysis is also similar to the earlier used examples of silver nanoparticle catalysis in aqueous and related organic reactions (Balwe et al., 2017; Wang et al., 2016).

Concerning the stereochemistry orientation, the anti-product is proposed to form preferentially in comparison with the syn-product due to the absence of steric hindrance between the substituents in the former case.



Scheme 2: Plausible Catalytic Reaction Mechanism

Conclusion

This study presents a sustainable method of synthesis of silver nanoparticles (AgNPs) using the fruit extract of Phyllanthus emblica (amla). The presence of different phytochemicals in the extract helped in reducing the silver ions and in the stabilization of the nanoparticles. Surface plasmon resonance (SPR) of the nanoparticles was observed in the form of characteristic absorption band in the UV-visible region at about 430 nm. Formation of AgNPs was further confirmed through the structural and morphological analysis. X-ray diffraction (XRD) analysis suggested that the structure of the nanoparticles is fcc crystal structure, whereas scanning electron microscopy (SEM), transmission electron microscopy (TEM) confirmed that the nanoparticles have the size of 10-25 nm.

Biosynthesized AgNPs showed good catalytic activity during the Knoevenagel reaction of isatin derivatives with rhodanine and 3-ethylrhodanine under aqueous conditions. Reaction time was found to be short while yield was quite good, suggesting the potential application of these plant-synthesized AgNPs as heterogeneous catalysts for this reaction. Successful recyclability of the catalyst proved its application for sustainable synthesis in the laboratory. Results of SEM, TEM, HRTEM, and XRD analysis show that the morphology and crystallinity along with surface characteristics of AgNPs due to phytochemicals might be responsible for their catalytic activity.

In summary, this study creates an actual link between the biosynthesis of nanoparticles via plants and organic catalysis using green chemistry principles. The use of the extract of P. emblica offers a relatively straightforward and eco-friendly approach to the formation of silver nanoparticles, as well as shows their utility in synthesizing isatin-containing heterocycles. However, more research needs to be done including control and comparison catalytic reactions for elucidating the exact role of metallic AgNPs, precursor molecules of silver, and phytochemicals from the plant extract. This will lead to a better understanding of the source of the mentioned catalytic properties.

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