Solar photocatalytically active, engineered silver nanoparticle synthesis using aqueous extract of mesocarp of *Cocos nucifera* (Red Spicata Dwarf)

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**ABSTRACT**

Silver nanoparticles synthesised using aqueous extract of *Cocos nucifera* (CN) mesocarp were evaluated for their photocatalytic activity under solar irradiation. The silver nanoparticles were synthesised by a green method of harnessing bioactive phytocomponents from the mesocarp of *Cocos nucifera*. Large-scale application of this process necessitates the manoeuvering of the process parameters for increasing the conversion of silver ions to nanoparticles. Process parameters influencing the morphological characteristics of silver nanoparticles such as precursor salt concentration and pH of the synthesis mixture were studied. The crystalline nanoparticles were characterised using UV-vis spectroscopy, XRD, FTIR, SEM and EDX analysis. CN extract and 5 mM silver nitrate solution at a ratio of 1:4 (v/v) in the synthesis mixture was found to be the optimum. Alkaline initial pH of the synthesis mixture was found to favour the synthesis of smaller sized monodispersed silver nanoparticles. Solar energy was harnessed for the photocatalytic degradation of Malachite green dye using silver nanoparticles obtained through the green synthesis method. Overall process aims at utilisation of naturally available resource for the synthesis of silver nanoparticles as well as the degradation of dyes using these nanoparticles, making it useful in the treatment of wastewater.

**1. Introduction**

Recent developments in the field of nanotechnology have led to the synthesis of metal and metal oxide nanoparticles through different routes. Noble metal nanoparticles of gold and silver exhibit enhanced properties based on their nanoscale size and structure enabling their usage in various applications [1–6]. These enhanced properties exhibited by nanoparticles are due to large surface-to-volume ratio, large surface energy and reduced imperfections. Synthesis of nanosilver is the most commercialised research area with a huge applicability sector, as silver nanoparticles (AgNPs) exhibit a myriad of properties such as antimicrobial [7], photocatalytic [8], optical [9,10] and electrical properties [11].
Benefitting from these properties AgNPs have found relevance in cosmetics [12], healthcare sector [13], water purification [14] and textile industry [15–17]. Of late, photocatalytic activity of AgNPs has been extended to the degradation of dyes [18–21] that constitutes as a major pollutant in the effluents from paper, textile, leather, food, cosmetic and pharmaceutical industries.

Plant-mediated synthesis route for the synthesis of AgNPs is considered to be a green and self-sustaining process with a low chemical footprint that overcomes the demerits of traditional physical and chemical routes of AgNPs synthesis [22]. In an attempt to nature mine the bioactive compounds that remain unharnessed, in the present paper the AgNPs were successfully synthesised by using the aqueous extract of the mesocarp of Cocos nucifera fruit (CN extract). The extract of mesocarp of Cocos nucifera fruit is known to contain phytocomponents [23–25] that exhibit antinociceptive, antioxidant, anthelmintic, anti-inflammatory, analgesic, antibacterial and antiviral properties [26–30] and also aid in the synthesis of AgNPs. The effect of precursor salt solution concentration and initial pH of the synthesis mixture on the morphological characteristics of AgNPs was also studied.

The synthesised AgNPs were further tested for the photocatalytic activity in terms of degradation of an azo dye under solar light irradiation to investigate its potential for use in the treatment of large quantities of industrial effluents containing complex organic compounds such as dyes. Malachite Green (MG) dye was used as a model dye for investigating the solar photocatalytic activity of AgNPs synthesised using CN extract.

2. Materials and methods

2.1. Processing of plant material

*Cocos nucifera* (CN) mesocarps were collected from the surrounding areas of Surathkal, Mangalore, positioned at 12°58′60 N, 74°46′60 E geographically in Karnataka, India. Freshly collected CN mesocarps were sliced and washed thoroughly under tap water followed by series of distilled water rinsing. CN mesocarps were shade dried and powdered using a domestic motor operated blade mixer. The processed powder was stored in air tight containers for further use.

2.2. Preparation of aqueous CN extract

The aqueous extract of CN mesocarp was prepared by boiling 5 g of powdered CN mesocarp in 100 mL of deionised water for 5 min through open solvent heating process. The extract obtained was filtered through Whatman No. 1 filter paper and the filtrate was stored at 4 °C in air tight bottles for further use.

2.3. Synthesis of AgNPs

Silver nitrate was used as the precursor salt for the synthesis of AgNPs. CN extract and silver nitrate solution of desired concentration were made to react in the volumetric ratio of 1:4. The reaction mixture was continuously agitated using a magnetic stirrer maintained at a temperature of 28 ± 2 °C for a period of 24 hours. Characteristic colour
change in the reaction mixture from light yellow to dark brown was monitored to provide an indication for the formation of AgNPs [31]. As metallic AgNPs are known to exhibit characteristic surface plasmon resonance (SPR) peak, SPR band of the reaction mixture was obtained using a dual-beam UV–vis spectrophotometer (Labomed, USA) at a scan range of 350–700 nm and scan speed of 1 nm and analysed for the formation of AgNPs.

2.4. Factors affecting the synthesis of AgNPs

In order to investigate the role of factors such as precursor salt concentration and pH on the synthesis of AgNPs, the synthesis was carried out by mixing CN extract and precursor salt solution in the fixed volumetric ratio of 1:4. The concentration of precursor salt solution and initial pH of the synthesis mixture were varied to study the effect of these factors on the synthesis of AgNPs.

2.4.1. Effect of precursor salt solution concentration on the synthesis of AgNPs

A stock solution of 100 mM AgNO₃ precursor salt solution was prepared and was diluted suitably to yield solutions of concentrations of 1, 2, 5, 7, and 10 mM. To evaluate the effect of concentration of precursor salt solution on the synthesis of AgNPs, the volumetric ratio of CN extract and precursor salt solution in the synthesis mixture was kept constant at 1:4 while the concentration of the precursor salt solution used in the synthesis mixture was varied. The mixture was continuously agitated at 28 ± 2 °C, for a period of 24 hours. A total of 300 μL of aliquots was drawn from the reaction mixture after a reaction period of 24 hours and was suitably diluted for the SPR analysis. The synthesis solutions containing AgNPs were then analysed for the characteristic SPR peak by using a dual-beam UV–vis spectrophotometer (Labomed, USA).

2.4.2. Effect of pH on the synthesis of silver nanoparticles

The pH of the synthesis mixture comprising the CN extract and the precursor salt solution at the optimum concentration (as obtained from the studies detailed in Section 2.4.1) in a fixed volumetric ratio of 1:4 was varied in a range of 3, 7, and 11 units and the synthesis was carried out at 28 ± 2 ºC for 24 hours. The pH of the synthesis mixture was set using 0.1 N HNO₃ and 0.1 N NaOH. Spectral analysis of the AgNPs synthesised under varying conditions of pH was carried out.

2.5. Recovery of AgNPs

The colloidal suspension of AgNPs synthesised was centrifuged at 15,000 rpm for 15 minutes. AgNPs obtained after centrifugation were washed with 70% ethanol and dried in hot air oven for a period of 24 hours at 120 ºC. The dried AgNPs were used for further characterisation and photocatalytic activity determination.
2.6. Role of bioactive compounds present in the CN extract on the synthesis of AgNPs

CN extract is known to contain many bioactive compounds which assist in the reduction of the precursor salt into AgNPs and also serve as capping agents. The antioxidants, flavonoids and phenolics present in the plant parts have been proven to reduce Ag$^{+}$ ions to zerovalent silver and thus, they are involved in the synthesis of nanoparticles [32,33]. Thus, to investigate the role of these compounds in the AgNP synthesis, the total antioxidants, total flavonoids and total phenolics present in the synthesis mixture before and after the synthesis were determined. Assays for the analysis of total antioxidant, total phenolic and total flavonoid content were performed by FRAP assay method, Folin-Ciocalteu method and spectrophotometric method of determining flavonoid–aluminium complex respectively and the detailed methodology is described elsewhere [34].

2.7. Characterisation of AgNPs synthesised using CN extract

Scanning electron microscope (SEM) and energy-dispersive X-ray (EDX) analysis, X-ray diffraction (XRD) analysis, transmission electron microscopic (TEM) analysis and Fourier transform infrared (FTIR) spectroscopic analysis were carried out to determine the shape, size and structure of the biosynthesised AgNPs.

2.7.1. SEM and TEM of AgNPs

AgNPs were drop coated onto carbon tapes and gold sputtering (JFC-1600 Auto fine coater, JEOL, Japan) was performed before carrying out the SEM analysis to analyse the morphological characteristics. The dried AgNPs were also analysed for their morphological characteristics by TEM (JEM 2100, Japan).

2.7.2. XRD analysis

X-ray diffractogram of the synthesised AgNPs was obtained using the X-ray diffractometer instrument (XRD, JEOL) at 20 range of 20°–100° using Cu Kα radiation at an operating voltage of 40 kV. Scherrer’s formula presented as Equation (1) was used to determine the crystallite size ($D_p$) of the nanoparticles.

\[
D_p = \frac{K\lambda}{\beta/2\cos \theta}
\]  

where $K = 0.94$ (constant), $D_p =$ average crystalline size, $\beta/2$ = the full width half maximum (FWHM) of the peak, $\theta =$ peak angle and $\lambda =$ X-ray wavelength (1.5418 Å).

2.7.3. FTIR analysis

The synthesised AgNPs were analysed on Jesco 4200 FTIR in the attenuated reflectance mode operating at a resolution of 4 cm$^{-1}$ in the mid-IR region of 400–4000 cm$^{-1}$ to determine the functional groups of the organic moieties present, if any on the surface of the biosynthesised AgNPs as capping agents. AgNPs were also analysed using FTIR after photocatalysis.
2.8. Solar photocatalytic activity of the synthesised AgNPs in terms of degradation of MG dye under solar irradiation

In the current study, the photocatalytic activity of the synthesised AgNPs was tested in terms of its efficacy to photocatalytically degrade MG dye. Photocatalytic degradation of MG dye at a concentration of 50 mg/L was carried out in 50 mL of aqueous solution using 10 mg of the synthesised AgNP powder. The reaction mixture was continuously stirred using magnetic stirrer under bright solar irradiation for 6 hours from 10 AM to 4 PM in the month of April. To test for any possible solar photolytic reaction, a control batch experiment was conducted under sunlight in the absence of AgNPs by maintaining the similar conditions as that of photocatalytic degradation experiments. An experiment was also conducted in the presence of AgNPs but under dark conditions, to test for any possible adsorption of the dye. Samples were withdrawn from the reaction mixtures at regular intervals of one hour and the dye concentration was determined through absorbance measurement at a wavelength of 614 nm using UV–vis spectrophotometer and the precalibrated data. Percentage dye removal or degradation was calculated using Equation (2)

\[
\text{Percentage degradation} = \left( \frac{C_0 - C}{C_0} \right) \times 100
\]  

where \(C_0\) is the initial dye concentration and \(C\) is the dye concentration at any time during the reaction. The chemical oxygen demand (COD) and total organic carbon (TOC) of the samples were analysed at intermittent time intervals to study the extent of mineralisation of the dyes. Measurement of COD was performed using APHA standard method [35] and TOC was analysed using Shimadzu TOC-VCSH (Japan) Carbon Analyzer. Percentage COD and TOC removal were calculated based on the initial COD and TOC levels.

3. Results and discussion

Plant-mediated route has been gaining momentum over time as it is considered an eco-friendly ‘green’ route of nanoparticle synthesis. In the present study AgNPs were successfully synthesised using the aqueous extract obtained from the mesocarp of the fruit of Cocos nucifera tree. The synthesis of AgNPs was confirmed by visual observation of the colour change in the reaction mixture from pale yellow to dark brown as presented in Figure 1. This change in colour as an indication for the synthesis of AgNPs is widely reported by the researchers [36–42].

3.1. Effect of precursor salt solution concentration on the synthesis of AgNPs

The effect of precursor salt solution concentration on the synthesis of AgNPs was studied by carrying out the synthesis at a fixed volumetric ratio of the extract and the precursor salt solution (1:4), but by varying the concentration of the salt solution from 1 to 10 mM. The SPR spectra obtained from the synthesised AgNPs at varying concentrations of precursor salt solution after 24 h of the reaction time are as shown in Figure 2. The pH of the reaction mixture was unadjusted and it was found to be 4.2. The presence of peaks in the spectra at precursor salt concentrations of above 2 mM is characteristic of the
synthesised AgNPs. The extract of Cocos nucifera mesocarp is known to contain bioactive compounds [43] that could be responsible for the reduction of silver nitrate into AgNPs. The occurrence of characteristic peak of AgNPs in the present study is an indication that the Cocos nucifera mesocarp also contains the bioactive components that have the capability to reduce silver nitrate to silver.

From Figure 2, it is also observed that the intensity of the SPR peak emanating from AgNPs synthesised using 5 mM of precursor salt solution was found to be the maximum in intensity with the peak being centred at 450 nm indicating the formation of large number of AgNPs [44,45]. The characteristic SPR peaks of metallic AgNPs are generally centred at 420 nm and the red shift observed in the case of AgNPs synthesised using 5 mM precursor salt solution indicates the formation of larger sized AgNPs [46].

The broadening of the SPR peak occurs due to the oscillations of higher order electrons when the particle size is above 100 nm [47].

The SPR peaks obtained from the AgNPs synthesised using 7 and 10 mM precursor salt solutions were found to be broad and low in intensity indicating less number of larger sized particles. Decrease in peak intensity may be due to the depletion of stable nanoparticles and the broadening of peak may also be due to the formation of aggregates. Higher
salt concentrations would have led to increase in destabilisation of the particles as indicated by the broadening of peak along with decreased absorbance which may be due to increased particle aggregation and sedimentation [48]. The broad SPR may also be due to the formation of large anisotropic particles [49]. When the concentration of Ag\(^+\) ions in the solution increases, large amount of reducing agents present in the CN extract are being utilised to reduce these Ag\(^+\) ions to AgNPs. It reduces the amount of bioactive components present in the medium extensively, thus changing the dielectric nature of the medium. The amount of capping agents present in the medium may also be not sufficient to form a capping around all the nanoparticles in the medium. Thus, the presence of a large number of nanoparticles changed the nature of the surrounding medium and the absence of sufficient capping around the nanoparticles led to collision of the particles and subsequent aggregation. Similar trend in the decrease of SPR peak intensity of AgNPs with increasing concentration of precursor salt (Ag\(^+\) ions) has been reported by Dubey et al [50]. Synthesis mixtures containing 1 and 2 mM of AgNO\(_3\) as precursor salt solution concentration did not produce a prominent SPR peak indicating the inadequate presence of Ag\(^+\) ions in the synthesis medium for the reduction by the plant bioactive compounds present in the CN extract to form AgNPs.

These studies indicate that the optimal precursor salt solution concentration for the synthesis of AgNPs using CN extract is 5 mM, owing to the formation of a large number of stable nanoparticles using extract and salt solution at a volumetric ratio of 1:4.

### 3.2. Effect of initial pH on the synthesis of AgNPs using CN extract

Careful manoeuvring of synthesis process parameters yields the desired characteristics of AgNPs; hence the initial pH of the synthesis mixture was varied to analyse the effect on the synthesis of AgNPs. The effect of pH on the synthesis of AgNPs was studied by carrying out the synthesis at a fixed volumetric ratio of the extract and precursor salt solution (1:4) and at fixed precursor salt solution concentration of 5 mM, but by varying the initial pH of the reaction mixture at pH 3,7,11 and unadjusted (normal). UV-Vis spectra of AgNPs synthesised under different conditions of initial pH of the medium shown in Figure 3 were analysed for their SPR peak characteristics. Figure 3 revealed that acidic pH

![Figure 3. SPR peaks obtained from AgNPs synthesised by reaction mixtures maintained at different pH.](image-url)
did not favour the formation of AgNPs as there was no prominent SPR peak observed. Prominent SPR peak characteristic of AgNPs was observed from the spectral analysis of AgNPs synthesised from the reaction mixtures with neutral and alkaline initial pH conditions. The SPR peaks emanating from AgNPs synthesised in neutral and alkaline pH were more intense, narrow and exhibited blue shift in comparison to the SPR obtained from AgNPs synthesised under the normal initial pH (normal pH range = 3.9–4.2 without adjustment) conditions of the synthesis mixture for AgNP synthesis. The peak is broader with normal pH indicating anisotropic particle formation and the red shift indicates larger size nanoparticles.

The SPR peak obtained with AgNPs synthesised at initial alkaline pH condition of 11 is centred at 414 nm, a blue shift of 40 nm from the maximum absorption of 455 nm obtained from AgNPs synthesised in the reaction mixture with the normal initial pH is observed. The peak of AgNPs synthesised under alkaline initial pH condition is narrower than the SPR peak obtained from the AgNPs synthesised at neutral initial pH. The decrease in the width of the SPR peak of AgNPs synthesised under alkaline initial pH along with the blue shift indicates the formation of small-sized monodispersed AgNPs [51–53] than the AgNPs synthesised under neutral and normal initial pH conditions. AgNPs synthesised under alkaline pH conditions are smaller in size and monodispersed. Alkaline pH favouring the synthesis of AgNPs has been widely reported [36,54,55]. As the pH of the medium is increased towards alkalinity, the electron density of the particle increases and the SPR peak is known to blueshift. The dispersity of the AgNPs also increases with the increase in the alkalinity of the reaction mixture. In an elaborate study conducted by Vimala et al. [56] it was inferred that the plant bioactive compounds are stable under alkaline conditions and this promoted the interaction between the Ag⁺ ions and the bioactive compounds, resulting in smaller and higher number of AgNPs. The morphological characteristics of AgNPs are apparently influenced by the process parameters governing the synthesis reaction. A better insight in understanding this can be derived from the SEM analysis of the AgNPs synthesised. Reports suggest that changing the pH condition of the medium confers a change in the size of the AgNP being synthesised. The SEM images of the AgNPs synthesised with normal initial pH of around 4.2 and at pH of 11 are shown in Figure 4(a) and (b) respectively. As seen in Figure 4(a) the AgNPs with normal pH (unadjusted condition) are polydispersed with a wide size range of around 200–500 nm and are anisotropic containing different shapes such as cubicle or spherical. However, the AgNPs synthesised with alkaline pH of 11 are spherical, monodispersed and ranged around 40–50 nm in size. The inference drawn through the SEM analysis was found to be in agreement with that of the spectral analysis data obtained from the SPR peaks in Figure 3. Thus, initial pH of 11 was found to be the optimum condition for the synthesis of AgNPs using CN extract.

As seen in Figure 4(a), (b) and (c), there is a significant reduction in the bioactive compounds such as antioxidants, phenolics and flavonoids, respectively, in the synthesis mixture after the synthesis of the AgNPs. The reduction of the bioactive compounds confirms their utilisation in the synthesis process for the reduction of the precursor salt (AgNO₃) to AgNPs and their subsequent role in capping, thus signifying the pivotal role of plant bioactive compounds present in the CN extract for the synthesis of AgNPs.
3.3. Characterisation of AgNPs synthesised using CN extract

AgNPs synthesised using optimum conditions such as 5 mM of AgNO₃ solution, alkaline pH condition of 11 and CN extract to precursor salt solution in the volumetric ratio of 1:4 were recovered from the synthesis mixture according to the procedure mentioned in Section 2.6 and characterised using SEM, TEM, XRD analysis and FTIR spectroscopy analysis. SEM image is shown in Figure 5(b) which indicates the formation of spherical, monodispersed nanoparticles with size ranging from 30 to 50 nm. TEM images of the synthesised AgNPs are shown in Figure 6. TEM images confirm the formation of spherical AgNPs with an average size range of 30–50 nm. A uniform capping around the nanoparticles is visible in the TEM, indicating that the phytocomponents in CN extract form a capping around the AgNPs.

XRD of AgNPs synthesised at the optimum conditions of synthesis is shown in Figure 7 and it revealed the face-centred cubic crystalline structure of AgNPs with peaks at 2θ values of 38.22°, 44.38°, 64.52° and 77.36° corresponding to the (111), (200), (220) and (311) planes, respectively. Average particle size was found from Scherrer’s formula to be 45 nm which is in agreement with the SEM and TEM results, indicating the formation of smaller-sized AgNPs under alkaline conditions.

The FTIR spectra of the AgNPs synthesised using CN extract was obtained in the fingerprint region ranging from 4000 cm⁻¹ to 400 cm⁻¹ and revealed strong absorption
bands located at 3294.79, 3017.09, 2929.34, 1739.48, 1617.98, 1519.63, 1438.64, 1367.28, 1220.72, 1029.8, 886.13 and 808.028 cm\(^{-1}\) as shown in Figure 8(a). The prominent peak at 3294.79 cm\(^{-1}\) resulted due to the stretching of the N–H bond amino groups and is the indication of bonded hydroxyl group present on the surface of the AgNPs as capping agent [57], peak 1617.98 cm\(^{-1}\) may be assigned to chelated carbonyl group or –OH from carboxylic group [58] and peak 1029.8 cm\(^{-1}\) suggests the symmetric C–O stretching. The band at 1739.48 cm\(^{-1}\) corresponds to C=O (phenols) and peak at 1367.28 cm\(^{-1}\) corresponds to S=O stretching vibration. The 1220.72 cm\(^{-1}\) band arises most probably from the C–O group of polyols such as hydroxyflavones and catechins [59]. It has been well reported that plant moieties are responsible in bringing about the reduction of Ag\(^{+}\) ions to AgNPs and capping of the AgNPs, while the same can be inferred through the FTIR analysis as well as the utilisation of plant bioactive components such as antioxidants, phenolics and flavonoids as discussed in Section 3.2 and depicted in Figure 4(a)–(c).

Figure 5. SEM analysis of AgNPs synthesised using CN extract at (a) normal pH of 4.2 and (b) alkaline pH 11.

Figure 6. TEM analysis of AgNPs as synthesised using CN extract.
**Figure 7.** X-ray diffractogram of AgNPs synthesised using CN extract.

**Figure 8.** FTIR spectrum of AgNPs (a) before their use in photocatalysis and (b) after photocatalysis of Malachite Green dye.
Thus, the FTIR spectra strongly suggests the presence of plant capping agents encapsulating the biosynthesised AgNPs and these capping agents have been hypothesised to undergo ionisation in the alkaline pH conditions and lead to the increase in the surface charge of the AgNPs by restraining the free electrons within a small volume [60]. This explains the formation of small sized, monodispersed and stable AgNPs.

3.4. Solar photocatalytic activity of the synthesised AgNPs in terms of degradation of MG dye under solar irradiation

MG dye was used as a model compound to test the solar photocatalytic activity of AgNPs synthesised using CN extract under optimised conditions of pH 11 and 5 mM silver nitrate solution with CN extract to silver nitrate solution in volumetric ratio of 1:4. AgNPs in the powdered form were employed to photocatalytically degrade 50 mg/L of MG dye under solar radiation at average light intensity of 943.5 \* 100 Lux. Experiments were also performed in the absence of AgNPs under solar radiation, as well as in the presence of AgNPs in dark conditions. Figure 9 presents the percentage of MG dye degraded using AgNPs under solar radiation. AgNPs were able to effectively degrade 75% of the dye under solar light, whereas in the absence of AgNPs only around 30% dye removal was achieved showing that the AgNPs are photocatalytically active under solar light irradiation. The experiment carried out under dark conditions revealed less than 10% dye removal, indicating minimal adsorption of MG dye on the nanoparticles.

AgNPs are known to absorb light in the visible range of the light spectrum due to its SPR characteristics. Wang et al. [61] stated that, Ag nanoparticles are good, highly efficient and stable photocatalysts under ambient temperature with visible light illumination for degrading organic compounds and dyes.

The crystallographic nature of the nanoparticles along with the morphological structure and size also plays a crucial role in determining the photocatalytic nature of AgNPs [21]. Kumar et al. [22] have reported the photocatalytic activity of AgNPs and have attributed it to the excitation of the SPR by visible light radiation, confirming that AgNPs are effective and stable photocatalysts under solar radiation. AgNPs hence can exhibit the

![Graph showing percentage degradation of MG dye](image)

**Figure 9.** Percentage of Malachite Green dye photocatalytically degraded using AgNPs synthesised using CN extract.
photocatalytic activity, opening new avenues in the field of photocatalysis by employing metal nanoparticles rather than the conventional semiconductor nanoparticles [62]. To further comprehend with the photocatalytic degradation of the MG dye, the AgNPs were recovered after dye degradation and subjected to FTIR analysis. The FTIR spectra as shown in Figure 7(b) obtained after photocatalysis ascertained a prominent shift in the absorption peak 3294.79 cm\(^{-1}\), in comparison to that of Figure 7(a). The peak corresponds to –OH (Hydroxyl) group and notably reduced after photocatalytic degradation, acknowledging the role of the capping agents. It can be summarised that the AgNPs absorb the solar radiation and lead to the excitation of electrons on the surface by the surface plasmon effect. The dye forms a complex with the capping agent at the surface of the AgNP which is in turn was photocatalytically degraded. As seen in Figure 7(a) and (b) there is no significant reduction in the capping agents encapsulating the AgNPs other than the hydroxyl group indicating that the AgNPs are stable even after the photocatalysis of the dye molecules under solar irradiation.

As seen in Figure 8, AgNPs serve as photocatalysts in the degradation of MG. According to the detailed study carried out by Chen and co-workers [63], AgNPs are known to photocatalytically degrade the organic molecule by absorption of visible as well as UV light of the solar spectrum.

When AgNPs absorb visible light of the solar spectra, the surface electrons from the outermost sp band are excited to a higher energy state due to SPR effect [64–66]; these electrons are readily accepted by the oxygen (O\(_2\)) molecules to form oxygen radicals (O\(_2^*\)) which attack and degrade the MG dye molecules. Also, the holes generated in the 5sp orbital are filled by the acceptance of electrons [63] from the adsorbed photosensitised dye molecule; thereby degrading the MG dye molecule. Absorption of UV irradiation from the solar spectra by the AgNPs causes the excitation of electrons from the 4d orbital to 5sp orbital. This interband transition leads to excitation of many photogenerated electrons. These excited electrons interact with the oxygen molecules to form oxygen radicals (O\(_2^*\)) and the hydroxyl ion to form hydroxyl radical (OH\(^*\)). Thus formed radicals attack the dye molecule adsorbed onto the surface of the AgNPs and bring about the degradation of the dye. In addition to the degradation of the dyes by the radicals, the holes generated in the d orbital of the AgNPs accept electrons from the adsorbed dye molecule leading to further degradation [63] of the MG dye. Thus, the AgNPs are known for absorption of whole of the light spectrum due to SPR effect and the interband transition of 4d electrons to 5sp band [67]. This mechanism of photocatalysis by UV and visible light irradiation by AgNPs in the degradation of MG dye is presented in Figure 10.

Figure 11 shows considerable reduction in TOC and COD levels during the photocatalytic degradation of MG dye. TOC and COD removal of 90.8% and 42.4% were achieved at the end of 6 h of irradiation period, indicating that the complex dye molecule is degraded to simpler products of less toxic nature. Continued irradiation for a prolonged period may further reduce the COD and TOC levels, thus leading to complete mineralisation of the dye.

The AgNPs synthesised using the extract of CN mesocarp were of size in the range of 30–50 nm and the size is comparable with those synthesised using other plant resources. AgNPs have been synthesised using different plant resources by various researchers. The comparison of AgNPs synthesised in the current study with those reported in literature by other phytochemical routes is presented in Table 1. It is observed that the AgNPs in
the current study are of similar or smaller size range than those reported by many other researchers. However, the plant resources used by these researchers possess agro-economical value and thus are not recommendable for AgNP synthesis. The present study utilises the resource which is an abundantly available agrowaste and thus it proves to be a sustainable process.

Figure 10. Mechanism of MG dye degradation using solar light active photocatalytic AgNPs synthesised using CN extract.

Figure 11. Percentage removal of TOC and COD levels during photocatalytic degradation of MG dye using AgNPs synthesised using CN extract.
The AgNPs synthesised in the current study are photocatalytically active under solar light and thus provide sustainable solutions for the treatment of dye contaminated wastewater. These nanoparticles are synthesised without the use of hazardous solvents or extreme conditions of temperature and pressure, thus exhibiting a lower chemical footprint on the environment. These AgNPs can be used for large scale treatment of wastewater by utilisation of solar energy, an abundantly available form of renewable energy. The synthesis of these AgNPs and their application as solar light active photocatalyst features energy efficient, ecofriendly and a green technology.

Conclusions

AgNPs were synthesised using the aqueous extract of mesocarp of *Cocos nucifera* fruit and engineered for desired morphological characteristics through optimisation of synthesis parameters. The morphological characteristics of AgNPs were influenced by the synthesis process parameters such as pH and concentration of precursor salt. Alkaline pH of 11 and precursor salt (AgNO$_3$) concentration of 5 mM were found to be the optimum conditions for synthesis of monodispersed AgNPs. The AgNPs synthesised with these conditions, were spherical, monodispersed and of average size range of 45 nm as analysed through SEM and TEM. The AgNPs were found to be crystalline with the average crystallite size matching the particle size. FTIR analysis confirmed that the bioactive phytocompounds are responsible in bringing about the reduction of Ag$^+$ ions and capping of the AgNPs. The synthesised AgNPs exhibited solar photocatalytic activity in terms of degradation of MG dye and the FTIR analysis of the AgNPs obtained after the degradation of MG dye confirmed the role of the capping agents in photocatalysis. The AgNP synthesis process is highly beneficial in terms of agro-biowaste utilisation and is a greener approach without the use of organic solvents. The AgNPs synthesised using CN extract exhibit their potential in application for wastewater treatment by photocatalytic degradation of dyes and other complex organic compounds under solar irradiation. Solar photocatalytic degradation of organic pollutants using AgNPs synthesised using an agro waste provides dual fold advantages of waste utilisation and energy efficient treatment of large quantities of dye containing effluents using solar energy.

Disclosure statement

No potential conflict of interest was reported by the authors.
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