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Eco-friendly production of silver nanoparticles from fenugreek seeds extract for organic pollutant degradation

Rajesh Kumar Meena[1*], Pragati Fageria[2] and Neelu Chouhan[1]
[1]Department of Pure & Applied Chemistry, University of Kota, Kota, Rajasthan, India
[2]Department of Chemistry, University of Rajasthan, Jaipur, Rajasthan, India
1988rajeshmeena@gmail.com

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Abstract

In the present research work, we report on the biosynthesis of silver nanoparticles (AgNPs) using seed extract of Fenugreek at room temperature. Synthesis of Plasmonic AgNPs is carried out by incubating the seed extract in presence of $AgNO_3$. Formation of AgNPs is confirmed by the appearance of a prominent surface plasmon resonance band in the Uv-visible spectrum at 425 nm. The biosynthesized AgNPs are characterized by Fourier-transform infrared spectroscopy (FTIR), powder X-ray diffraction (PXRD) studies, scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Further, the biosynthesized AgNPs are investigated for their catalytic, electrocatalytic and phenol remediation properties. As-synthesized Ag NPs were tested for their catalytic reduction activity towards the conversion of p-nitro phenol to p-aminophenol in excess of $NaBH_4$. The investigations revealed that the biosynthesized AgNPs excel in their respective applications. Based on the results, present study concludes that AgNPs can be biosynthesized using seed extract of Fenugreek and further can be employed for applications in electrochemical sensing, dye degradation and phenol remediation.

Keywords: Fenugreek**,** XRD, FTIR, FESEM and TEM etc.

Introduction

In recent years, the increase of toxicity free metal nanoparticles has become a great challenge in that times so noble metal nanoparticles like as Ag, Au, Pd and Pt have been extensively studied and suitable to their unique properties like as a optical, mechanical, electronic, magnetic as well as chemical that are extensively altered from bulk resources. These NPs individual and exclusive properties could be certified to their small size as well as bigger size zone. Present specific reasons are think about for metallic nanoparticles have start uses in many applications in similar kind of way such as a photonics, catalysis and electronics. Synthesis of AgNPs has involved mostly significant attention to their specific properties and uses, like electrical conductivity, optical with magnetic and polarizability, antimicrobial as well as antibacterial activities, catalysis, surface-enhanced Raman scattering (SERS) and DNA sequencing, as well as various field have been employed for the production of metal NPs. A number of processes have been devised in order to arrange metallic NPs. For case in point, one of the existing methods crystalizes nanoparticles in microemulsions using a array of chemicals as precursors and large amounts of surfactants as stabilizing agent. The similar preparation method like as a UV light irradiation[1,2], microwave irradiation process[3,4], chemical reduction method[5-7], photo chemical process[8,9], electron light irradiation[10,11] and sonoelectrochemical method[12] have been doing well in the synthesis of different type of nanoparticles materials: metallic[13-15], dielectric[16,17], semiconductor[18,19], and magnetic[20,21]. However, the intensive use of solvents and synthetic reactants is harmful for the environment. Mostly methods are actually costly and also entail the use of toxic and hazardous chemicals, which may pretence potential ecological and natural risks. For these reasons, it is very attractive to plan alterative, "green" process of nanomaterial research that uses eco friendly reactants. Since noble metal NPs are broadly valuable to areas of human being and so many different kinds of ways, there is a increasing want to extend ecofriendly process for NPs production that do not consume poisonous chemicals. A expedition for an environmentally sustainable production process has led to a small number of bio mimetic application.

A single creative process in bio mimetic fabrication involves in bio reduction process. Biological synthesis process of nanoparticles using like as a enzymes, Fungus, plant extracts as a stem, root, leaf, seed and fruit and microorganisms have been recommended as probable ecofriendly alternative to chemical and physical methods. Occasionally the synthesis of nanoparticles using involved processes of maintaining microbial cultures, so the synthesis of metal nanoparticles using plant extracts stems is an important role in remediation of hazardous metal during reduction of the metal ions. Silver nanoparticle are produced by different parts of the herbal plants like bark of neem leaves, Citrus limon, Tannic acid, Cinnamon and a variety of plant leaves. Among the noble metal nanoparticles like as Ag, Au, Pt, Pd, but silver nanoparticles have involved other than more interest for their benefit on a variety of studies such as catalysts, photosensitive components, and surface enhanced Raman spectroscopy etc.

Inside this research work, we characterized and synthesis of stable AgNPs from bio reduction method by using fenugreek plant seed extract. We synthesized the silver nanoparticles by the reaction of silver nitrate solution mixed with fenugreek seed's extract. Fenugreek seeds are the most useful part of fenugreek plant. These seeds are golden-yellow colour; small in size, structure[22] in fenugreek, saponin and alkaloids are anti-nutritional factors are present. Which are responsible as a reducing agent as well as a stabilizing agent for synthesis of silver nitrate solution to AgNPs[23].

The synthesized produce material was characterized by X-ray differaction (XRD), transmission electron microscopy (TEM) respectively. The results showed that the synthesized nano particles average diameter and spherical shape about 10-20 nm.

Materials and methods

The fenugreek plant seed were stored from medicinal garden of Agriculture university campus, Kota, India. The collected seeds were carefully washed by deionised distilled water then dried and crushed. Then the synthesized powder was advance used for research of 10 g/L aqueous seeds extract then filtered and kept at 4^oC in refrigerator until further utilize for current investigation. The extract is used within 7 days.

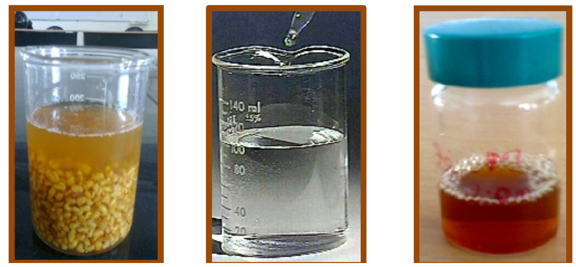
Required Chemicals: $AgNO_3$ 99% was purchased from Sigma-Aldrich (USA). We have deionised distilled water was used them during this process. All of the chemicals used in the study are of analytical grade and used without any purification.

Synthesis of silver nanoparticle: The required amount of fresh fenugreek seed extract was collected by firstly weighing 2gm fresh fenugreek seed in 100 ml beaker with in 50 ml of distilled water at room temperature for 24 h. The solution was filtered then secondly 2.0 ml plant seeds extract was mixed with 25 ml of freshly prepared 10^{-3} M silver nitrate solution kept at room temperature. The reaction mixture will be observed the colour change from light yellow to dark brown appeared during this process. The synthesized Ag nanoparticles dry at 90^oC temperature for further characterization.

Characterization of synthesized AgNPs: The synthesised AgNPs were optically observed by UV-vis spectroscopy over a range between 200 to 800 nm. The morphology of the synthesized AgNPs was observed by SEM investigation. FTIR was performed to achieve wide spectrum of nanoparticles were approved and classify the possible molecules that responsible for capping and reducing agent for the synthesis of AgNPs by fenugreek seed extract. The XRD result was analysed to note the purity of the sample, average particle size, crystallinity of sample and plane of the synthesized silver nanoparticle.

Results and discussion

Visual analysis: A transform of colour observed starting pale yellow to reddish brown in the solution after irradiation due to effect of surface Plasmon resonance.



(A) (B) (C)

Figure-1: Seed extract (A) Pure silver nitrate solution (B) Synthesized solution of AgNPs (C).

UV-visible analysis: One of the most usually used UV-visible spectroscopy techniques for description of synthesis and particle size of silver nanoparticles. Show the result of UV absorption spectrum (Figure-2) of the synthesized reddish-brown AgNPs solution through the proposed way showed a surface plasmon absorption band with a maximum absorbance of 425 nm, signifying the existence of small rounded size AgNPs. The spherical size morphology and structure was confirmed through FESEM (Figure-4). Time duration an important role in during the nanoparticle synthesis, this reason induce the reactivity of seed extract with silver ions. The influence of time duration in the AgNPs was evaluated under different time of the reaction mixture (Figure-2). In 6h small with broadening SPR band was formed indicates formation of large size of nanoparticles. After 12h, 18h and 24h the sharpness of peak increasing with increasing time duration. These results are indicates formation of spherical shape of silver nanoparticles. Several results are reported, time is important role for shape and size controlled silver nanoparticles. The present analysis indicates 24 h time duration is more suitable for complete synthesis of silver nanoparticles.

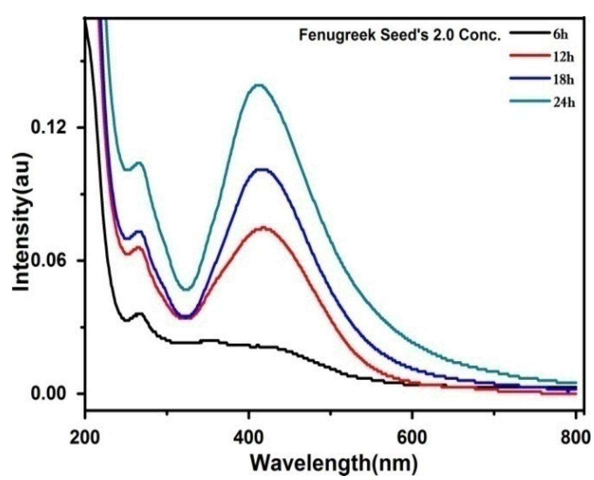


Figure-2: Uv vis. spectrum of synthesized AgNps.

Particle size analysis: The synthesized AgNPs solution obtained by centrifuged instrument, and which the material of AgNPs was dispersed in deionised distilled water to find a clear of several uncoordinated biological material solution. The purified material was then dried in oven at 90^{o}C temperature for 24 h, then the synthesized AgNPs powdered further used for FTIR, XRD, FESEM and EDX analysis.

X-ray diffraction analysis: XRD patterns for AgNPs synthesized by fresh fenugreek seed extract mixed with silver nitrate. Figure-3 shows most intense distinguishing diffraction peaks of Ag were appear at 2θ = 27.3, 29.7, 34.4, 45.0 and 53.9, which peaks are indicted of fcc (face centered cubic) AgNPs crystals, respectively (JCPDS 00-004-0783). No other bogus peaks from any phase were generated that the clear synthesized AgNPs had a spherical structure have been obtained directly. In wide-ranging, the XRD peaks width is related to crystallite size of AgNPs. Debye Scherrer equation was helped to find out average particle size from half width of the diffraction peaks.

$$D= (K\lambda)/(\beta\cos\theta).$$

Where D is signify of crystallite size of powder sample, λ is the wavelength value of Cukα, β is the significance of full width at half maximum, θ value is the responsible for bragg diffraction angle and k is a constant value. According Debye Scherrer equation, the synthesized regular size of AgNPs is originated to be 3.42 nm. The experimentally shows the peak enlargement and noise were most probable associated to the result of synthesized AgNPs and the existence of a variety of crystalline biological macromolecules in plant extracts which are responsible for these peaks. The observed results express that Ag ions had definitely reduced to Ag^0 by fenugreek plant seed extract under suitable reaction conditions.

TEM, SEM and EDX studies of AgNPs,: In the direction of increase and advance close the quality of the AgNPs, study of the synthesized sample was performed by SEM, TEM and EDX techniques. The elemental chemical investigation of the AgNPs was analysed by EDX on the TEM. Over all the EDX result of binding energies shows that no bogus peaks are related to impurity was observed. So the results are indicating that the obtained reaction product was highly pure. Transmission electron microscopy (TEM) was used to observe for morphology as well as provided the study of particle size details of the synthesized AgNPs.

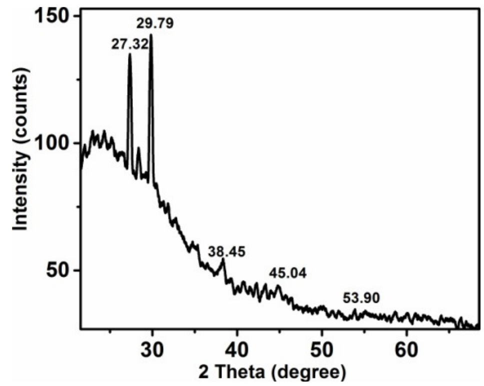


Figure-3: XRD Spectrum of synthesized AgNPs.

ATR Analysis: ATR measurement capacity was passed out to recognize the probable plant biomolecules extract which are accountable for reducing and capping agent for the synthesis of AgNPs. These apparent infrared bands are experimentally analysis at 3330 cm^{-1}, 1635 cm^{-1} and 580 cm^{-1} (Figure-5). In which strong broad band at 3330 cm^{-1} is appropriate for O-H and N-H band. The middle intense band at 1635 cm^{-1} come out from the C=O stretching manner in amine functional group which is usually create in the protein, representative the existence of proteins as capping agent for AgNPs which are liable for increases the stability of the synthesized AgNPs. Another one the intense and broad peak at 580 cm^{-1}and 557cm^{-1} responsible for Ag metal.

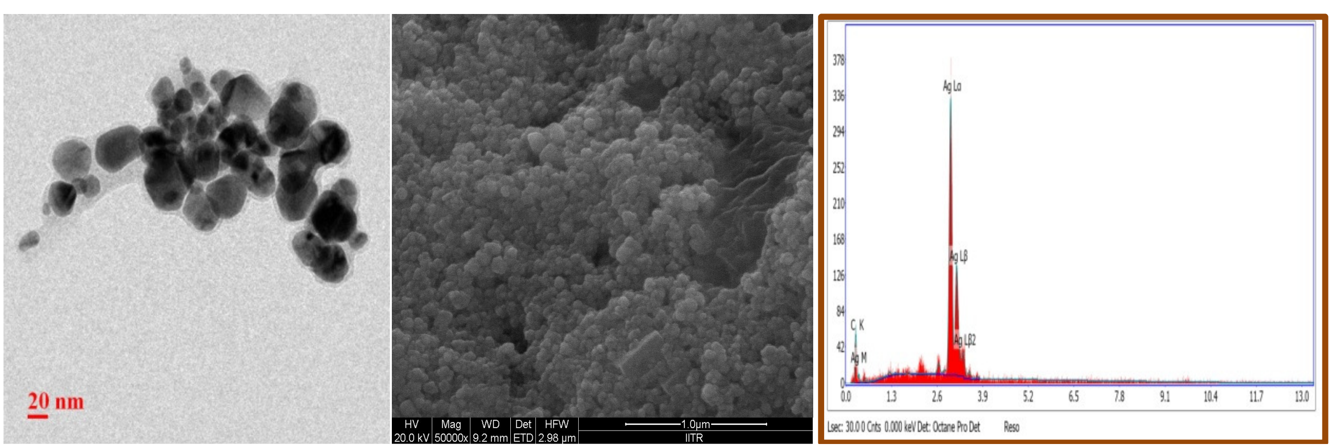


Figure-4: (a) TEM image and particle size distribution of AgNPs (b) FESEM images of silver nanoparticles, (c) corresponding AgNPs EDX profile.

Catalytic reduction of p-nitrophenol using $NaBH_4$ and AgNPs: 4-NP and its derivatives are common organic pollutants, used to manufacture herbicides, insecticides and synthetic dyestuffs, and they can substantially harm the ecosystem. The reaction product, 4-AP is enormously functional and important in many applications, used as an intermediate for manufacturing analgesic corrosion inhibitor, photographic developer, antipyretic drugs, anti-corrosion lubricant and hair-dyeing agent.

In present scenario, mainly useful applications of the AgNPs are to catalyze a number of chemical reactions which are kinetically challenged by nature. To assess the catalytic activity of the synthesized AgNPs, the reduction reaction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) with excess $NaBH_4$ is generally employed as a model reaction. A primary reason for selecting the 4-NP reduction reaction is that a reaction progress is easily monitored by using UV-visible spectrophotometry. Here Ag NPs were used for the reduction reaction using 0.05 mM 4-NP and 15 mM borohydride was introduced as a reducing agent. The progress of the reaction was determined by spectrophotometrically and the absorption spectra are calculated at various time intervals. Pure 4-NP has the absorbance at 300 nm and when $NaBH_4$ was added to 4-NP, the solution changed the colour from light yellow to dark yellow. It was observed from the UV-vis spectrum of this solution that the plasmon absorption band for the 4-NP is red shifted to 401.5 nm due to the formation of 4-nitrophenolate anions, which is experimentally justified by Figure-1. The peak positions remained unaltered still after the month due to large kinetic barrier for the reduction procedure, which signified that no reduction occurred without catalyst. Interestingly, on applying a fresh sample of biogenic AgNPs (0.1 mL, 100 mgL^{-1}) to this reaction mixture, the intensity of the 401.5 nm absorption peak (nitrophenolate ion), start decreasing. Concomitantly, a new peak appeared around at 300 nm wavelength, and increased with reduction time, confirming the formation of 4-AP. Finally the absorbance levels of 4-NP off, which indicates the end of the reduction reaction. The overall reaction proceeds within 18 min in the presence of as synthesized Ag NPs. On the other hand, a longer reaction time of 50 min was required to complete the reduction using silver solution as a catalyst which is equivalent of Ag atoms.

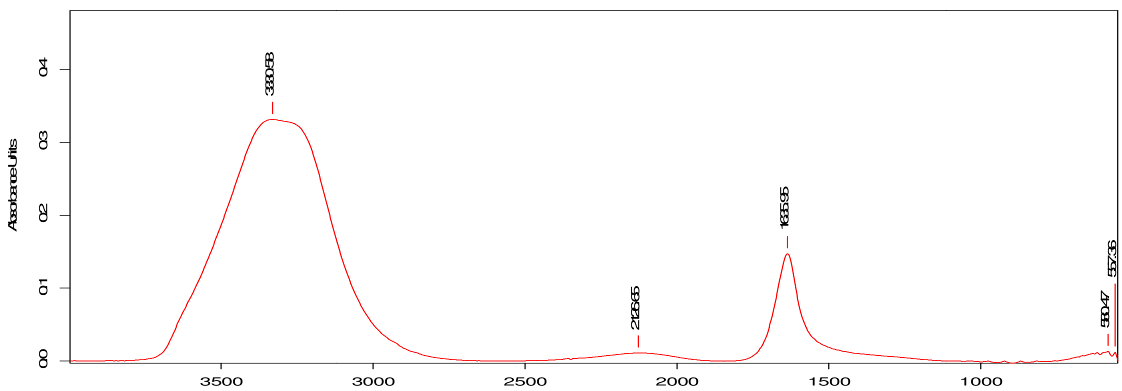


Figure-5: ATR spectra of AgNPs by Fenugreek plant extract.

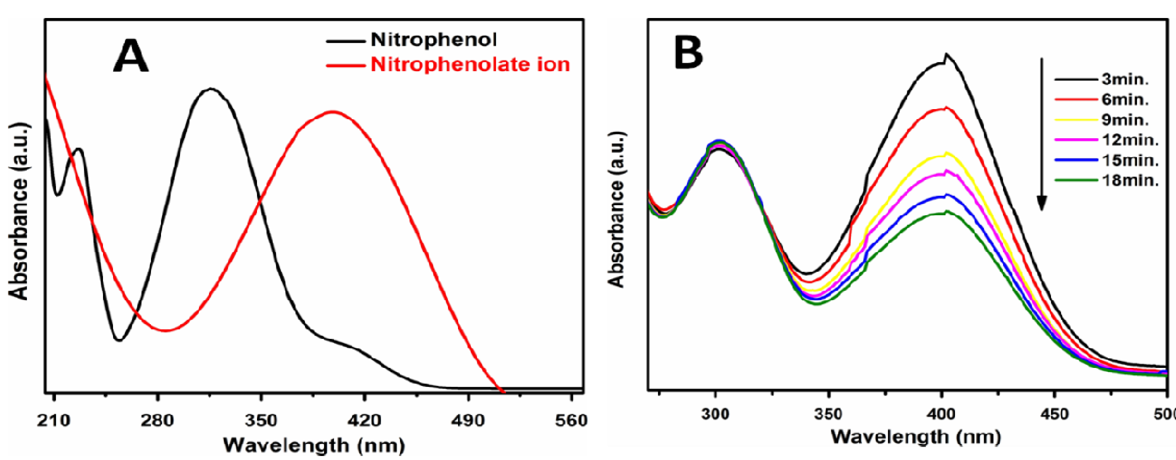


Figure-6: (A) UV-vis spectra of pure 4-nitrophenol (B) reduction of 4-nitrophenol to 4-aminophenol with time interval in presence of Ag NPs.

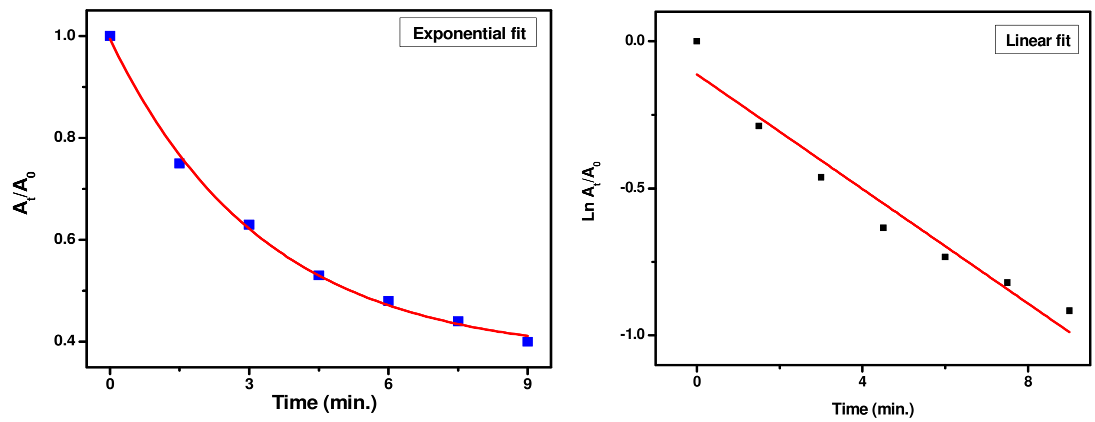
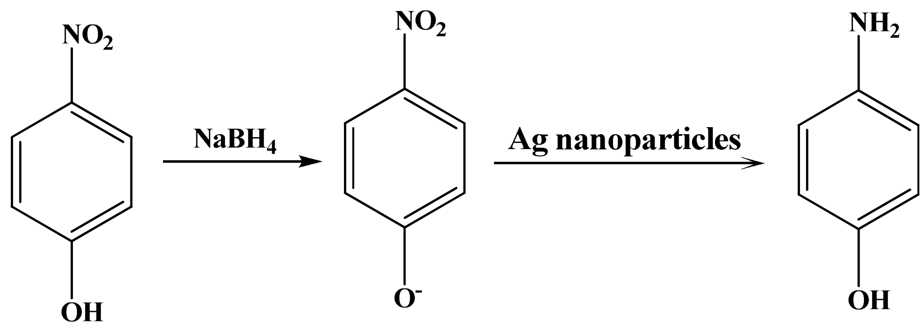


Figure-7: UV-vis spectra of 4-nitrophenol reduction in presence of Ag NPs (A) A_t/A_0 vs. time (min) plot (B) ln (A_t/A_0) vs. time (min) plot.



4-Nitrophenol **4-Nitrophenolate ion** **4-Aminophenol**

Figure-8: Overall Nitrophenol Reduction Mechanism.

This reduction reaction follow pseudo-first-order rate kinetics with respect to 4-NP. As the concentration of $NaBH_4$ was 300 fold greater to that of 4-NP, the catalytic rate constant (*k*) can be designed assuming a pseudo-first-order rate kinetics with respect to 4-NP. Figure-7A, shows the exponential relation between (A_t/A_0) *vs* 't' and linear relationship between ln (A_t/A_0) *vs* 't'. The catalytic rate constant (*k*) for the reduction reaction was calculated from the slope of the linear curve shown in the Figure 7B and the value is 1.5×10^{-1} min^{-1}.

The complete reduction of 4-NP to 4-AP is concise by the following equation: The reduction of organic pollutant 4-NP was completed within 18 min time duration upon the addition of synthesized AgNPs shown in Figure-6B. Eventualy bleaching of the yellow green colour of the reaction mixture confirms the formation of 4-AP. The reproducibility of the product was tested for replicates to verify the enhanced catalytic activity of AgNPs. FESEM Figure shows the study of the experimental data using different kinetic models, representative that the first order reaction model is largely accurate for the 4-NP catalytic reduction system.

Conclusion

Inside their research work the production of AgNPs by biological plant reducing method. Extract of fenugreek act as a green without chemical free non hazardous reducing agent. Which are responsible for synthesis of nanosize silver nanoparticles as well as stabilizer agent for the nucleation of AgNPs in cubes like structure. During the biosynthesis of the Ag nanoparticles, self-assembling of the chemical components of the fenugreek seed extract's around the of Ag^+ ion that leads the reduction of Ag+ ion to Ag NPs. The synthesized AgNPs were subjected to investigation such as different types of instrument like as a Uv-visible spectroscopy, FTIR, SEM and XRD, in order to characterize them. XRD studies confirmed the purity of these nanosized NPs that crystallized in a cubic and rod shaped crystals. To the excellent of our information this is the best observation of the unique structures of fenugreek seeds extract mediated AgNPs. The synthesised AgNPs have shown more important for organic pollutant degradation. Further studies using nano particles against cancer cell lines needs to be investigated.

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