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Biosynthesis of Silver Nanoparticles and its Utilization in Dye Decomposition for a Clean Environment: A Step Towards Sustainable Development

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Abstract

The tremendous interest of silver nanoparticles for the scientific community has cultivated due to its wide range of industrial applications including bio medicine. Silver (Ag) nanoparticles (NPs) are also being applied as an anti-carcinogen. Enumerable modes are available on its various synthesizing strategies which causes an adverse effect on environment. But green synthesis method which is either plant mediated or microbe mediated, a precious gift to the environment dedicated by the researchers. Here an eco-friendly approach for the preparation of Ag NPs by using aqueous extract of Neem leaves is reported. The formations of silver nanoparticle were confirmed by optical absorption spectra showing a broad absorption peaks at ~420 nm. This peak arises due to the absorption of incident light by the free electrons in the surface of the nanoparticles when they excited by an appropriate electromagnetic excitation. Material identification and crystallinity were dealt with X-ray diffraction spectra. The particles are found to be highly crystalline with face-centred cubic structure. The size of the particle was estimated by transmission electron microscope and found in the nanometer (10^{-9} m) scale. The synthesized nanoparticles showed a strong photocatalytic activity through the degradation of methylene blue dye under sunlight illumination. After four hours of sunlight irradiation the dye degradation was found to be 88%. The biosynthesized silver nanoparticles can be used in waste water treatment in a cost-effective way.

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Sustainable Development.

Introduction

Synthesis of material in the nanometer scale is the remarkable discovery in the twentieth century. The word “Nano” derives from the ancient Greek word “nanos” which means “dwaft”. Nano refers to one billionth. Nanometer (nm) can be felt by saying that a human hair is about one million nm wide. A material is called nanomaterial when at least one

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of its sides belongs to 1-100 nm. Nanomaterials show significantly different physical and *chem*ical properties in comparison to their bulk form. For example, the opaque material turns transparent (e.g. copper), insoluble becomes soluble and *chem*ically inert substance acts as an efficient catalyst (e.g. gold) when they are in nano form.[1] Metal nonoparticles (NPs) offer uniqueness in optical properties as because of surface plasmon resonance absorption. The thrilling colour of the nanomaterial appears not only due to its size or shape but also due to the dielectric medium surrounding them. The gold is yellow when in bulk form but the colour of gold colloid changes from ruby red to bluish as soon as the size of the particle varies from 20 nm to 200 nm, respectively.[2]

Noble metal NPs such as platinum, palladium, gold and silver (Ag) receive much attention because of their promising applications in advanced technology.[3] Among these metal nanoparticles, Ag has been chosen in promising biomedical application due to its high stability, cost effectiveness and high efficiency in contrast to the rest.[4] Apart from the increasing industrial use of Ag NPs, they are equally used in different medical applications including imaging, hyperthermia of tumours, drug delivery and even as an anti-carcinogen.[5]

The increasing global population with rapidly mutable microbial pathogens necessities the inevitable discovery of novel drugs to combat against human diseases. Also, the indiscriminate production and unscientific use of drugs without proper medical advice results in emergence of multiple antibiotic resistant strains (MARS) producing the more complicated issues of health hazard.[6] So, it is an alarming state for the scientists to develop novel drug for fighting against MARS. In this context, nanomaterials were paid much attention by the researchers due to their strong antimicrobial action, smallness in size resulting higher surface area, and strong binding affinity with microbes .[7] From the long past silver was utilized as a competent antimicrobial material used in medical purposes.[8] Ag NP sets its goal as it exhibits significant antimicrobial effect against a wide variety of microorganisms.[9]

For synthesizing Ag NPs a lot of methods are available few of which are laser ablation, pyrolysis, *chem*ical method, microwave assisted method, hydrothermal method etc. [10] Each of these methods suffers one or more drawbacks which include cost effectiveness, energy consumption, utilization of toxic *chem*icals such as capping and stabilizing agents, organic solvent and hence none is sustainable. To overcome this problem a new synthesis method called green synthesis method following the green *chem*istry to synthesize Ag NP is a sustainable way for better future.[11,12] Here in this method no toxic *chem*ical was used and hence it is environment friendly as well as cost effective. Green synthesis method is either plant mediated or microbe mediated.[13] Due to the cultural hazards of microorganisms, researchers usually prefer to use different parts of various plants as green materials for synthesizing nanomaterials. Ag NPs have already been synthesized by us using both the aqueous extracts of Neem and Guava leaf separately.[12,14] In this study we report the formation of Neem leaf extract mediated Ag NPs prepared at normal temperature using the aqueous solution of only one *chem*ical which is silver nitrate. The formation of Ag NP was confirmed by optical absorption spectra whereas the size of the particle was estimated by capturing the image of the particles by a transmission electron microscope. The results of all the experiments confirm that the Ag NPs were synthesized successfully in this sustainable green synthesis method.

During the last few decades the water is getting polluted by the organic dyes discharged from various industries leading to an untoward effect in environment as well as human health.Although a large number of methods like filtration, coagulation, ozonation, adsorption, anodic oxidation, reverse osmosis, etc. are being available for the removal of the toxic dyes, they all are not cost-effective.[15] Recently, the removal of methyl red dyes from aqueous solution using a novel hybrid absorbent PANI@Fe-Mn-Zr[16] and $MgFe_2O_4$/polyaniline nanocomposite[17] has been reported. A quick and enhance separation of the toxic dye Eosin Yellow from its aqueous solution has been achieved by coagulation method using ferric chloride as a coagulant.[18] So there is a growing demand towards a fast, improved, effective and low cost method for the removal of the hazardous dyes. Recently, green synthesized metal NPs has been used for the decomposition of different dyes such as methylene blue, rhodamine B, methyl red, 4-nitrophenol, congo red, and methyl orange.[19] However, the work claims its novelty as a significant percentage (~88%) of degradation of methylene blue (MB) dye under sunlight illumination has been achieved by using biosynthesized Ag NPs prepared by following the green *chem*istry.

Synthesis and Characterization

The s*chem*atic diagram for synthesis of biogenic Ag NPs is shown in figure 1. Fresh Neem leaves were collected from the local area and were washed properly. The leaves were sun dried and then crushed into powder. Approximately 5 gm of leaf dust was added in 0.1 liter distilled water and was kept at 45º C inside in a hot air oven till the water turns into light yellow. The coloured extract was then filtered properly and preserved in a refrigerator. The preparation of the sample is same as described in our previous work.[12,14] Here 2 ml leaf extract was added in 40 ml aqueous solution of silver nitrate (5mM) and the mixture was stirred continuously. After a while, the colour of the colourless mixture gradually turns into light yellow and then blackish yellow confirming the formation Ag NPs.

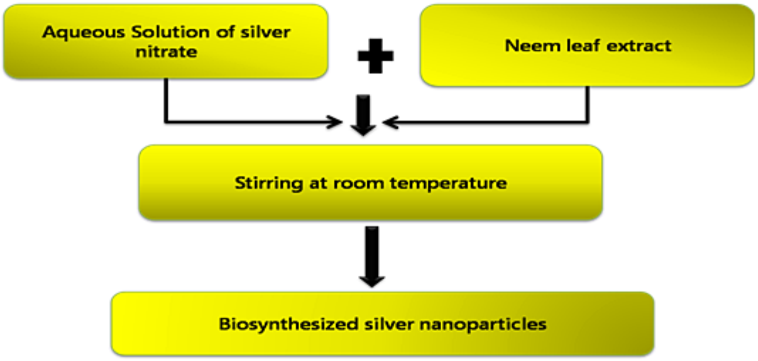

Fig. 1: Schematic diagram showing the synthesis of biogenic Ag NPs

Optical absorption (OA) spectroscopy measurements were performed using UV-Vis spectro photometer (JASCO, V-630). The crystal structure of the sample was studied through X-ray diffraction(XRD) techniques. Here PROTO AXRD diffractometer was used. It was functioning at 0.6 kW with operating X-ray wavelength 1.540 Å (CuKα radiation). For recording the XRD data, film was made by putting a couple of drops of the liquid sample on a cleaned glass substrate. The images of the particles were obtained by using a transmission electron microscope (JEOL, JEM 1400 plus).[12,14]

Study of Dye Degradation Activity

The dye degradation mechanism of these Ag NPs was performed on methylene blue dye under sunlight illumination. The dye solution was made by mixing 1 mg methylene blue in 0.2 liter distilled water. Then 5 mg of Ag NPs was added into the solution and mixture was stirred for 30 minutes in a dark chamber. The solution was then kept under sunlight illumination with continuous stirring. At a particular time interval some amount(~2 ml) of coloured water was isolated from the mixture and OA study was performed. The recording of data of this degradation was done by JASCO, V-630UV-Visible spectrophotometer.[20]

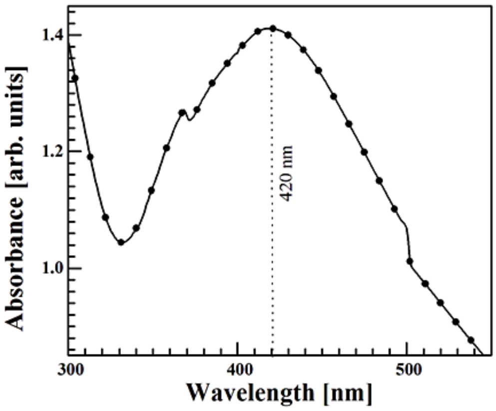

Fig. 2: OA spectrum of biosynthesized Agnanoparticles

Experimental Result

Optical Absorption (OA) Spectroscopy

At the time of preparation of sample, a gradual colour change of the aqueous sample was noticed as already discussed. Such change in colour confirms the formation Ag NP with different sizes. The formation of Ag NP can be confirmed by measuring the OA spectra of the coloured aqueous sample. It is the most essential and elementary techniques. Figure 2 shows the OA spectrum of the synthesized sample after 2 hours of adding Neem leaf extract in the silver nitrate solution. The spectrum contains a broad absorption peak centered at ~420 nm which confirms the formation of NPs of Ag. This absorption also called surface plasmon resonance (SPR) arises when the unbound electron on the metal surface oscillates harmonically when excited by electromagnetic radiation.[21]

TEM Studies

The direct measurement of size of the NP is done using the image as obtained from transmission electron microscope. Figure 3 shows the corresponding image where the particles are found to be nearly spherical. It is estimated that the average size of the synthesized sample is 30 nm.

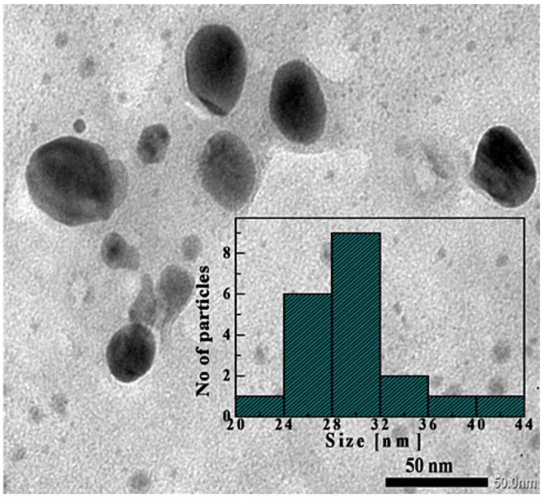

Fig. 3: TEM image of biosynthesized Ag nanoparticles

XRD Studies

Material identification and crystallinity of the material was analyzed by X-ray diffraction (XRD) spectrum. Figure 4 shows the XRD spectrum of the sample. The spectrum consists of four prominent diffraction peaks at ~ 38°, 44°, 54° and 78° corresponding to (111), (200), (220) and (311) planes of Ag.[22] The diffraction peak marked as (*) arises due to presence of biomolecules[23] within the sample. This result confirms that the synthesized sample is face-centred cubic and well crystalline structure. From XRD data mean grain size of particle is estimated as~20 nm.[23]

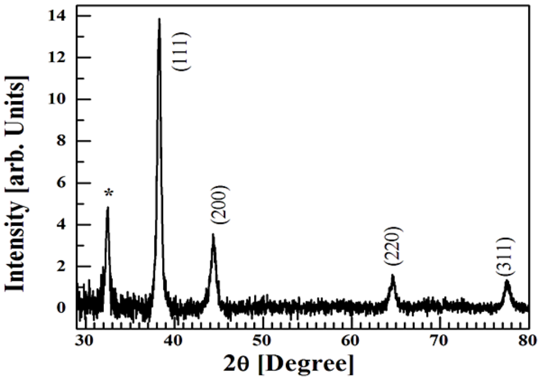

Fig. 4: XRD spectrum of biosynthesized Ag nanoparticle

Energy Dispersive X-ray Spectroscopy (EDS) Study

Figure 5 shows the EDS spectrum the synthesized sample. The spectrum contains a strong peak of Ag confirming the *chem*ical composition of the synthesized sample. The other small peaks of C, O and Cl in the EDS spectrum may due to the X-ray emission from biocompounds responsible for stabilization of the nanoparticle present in the sample.[24] The obtained result is in line because Ag NPs usually show a characteristic OA peak at around 3000 eV because of SPR.[25]

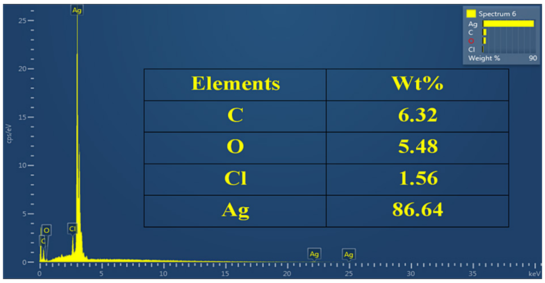

Fig. 5: EDS spectra of green synthesized Ag nanoparticle

Evaluation of Dye Degradation

The study of photocatalytic activity was performed on the decomposition of MB in sunlight illumination. Figure 6 shows the degradation of the dye at different time. Each spectrum consists of two OA peaks centered at ~663 nm and ~610 nm which ascribes the transitions of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi$, respectively.[26] The intensity of the absorption peaks steadily decreases with time which means that the biogenic Ag NPs decompose the dye and degrade it.

The percentage of degradation of the dye is estimated by using the equation as follows[27]

Degradation = $C_o - C / C_o$

Where C_o and C are respectively the concentration of the dye at time t=0 and at any time t.

The concentration of MB dye is proportional to the absorbance. Figure 7 shows the variation of percentage of dye degradation with time. It is observed that the dye degrades up to 88 % in four hours which infers the excellent performance of biogenic Ag NPs as a photocatalyst. Table 1 shows a comparison study of previously reported result with the present result on green synthesized Ag NPs mediated MB dye degradation in presence of sunlight. From the table it can be concluded that our green synthesized Ag NPs exhibited better photocatalytic effect in comparison to others.

Table 1: Comparison of Ag NPs mediated MB dye degradation in sunlight illumination of present study with some previously reported result

Extract used for Ag NPs synthesis	Concentration of MB dye (mg/l)	Concentration of Ag NPs (mg/l)	Time (hour)	Degradation (%)	References
Casuarina equisetifolia	1	100	5	35-40	[28]
Morindatinctoria	10	100	72	95.3	[29]
Pomegranate peel	10	100	48-72	89	[30]
Durio Zibethinus seed waste	10	100	3	73.49	[31]
Natural honey	10	100	72	92	[32]
Prosopis farcta fruit	10	500	4	86.38	[33]
Neem leaf	5	25	4	88	This study

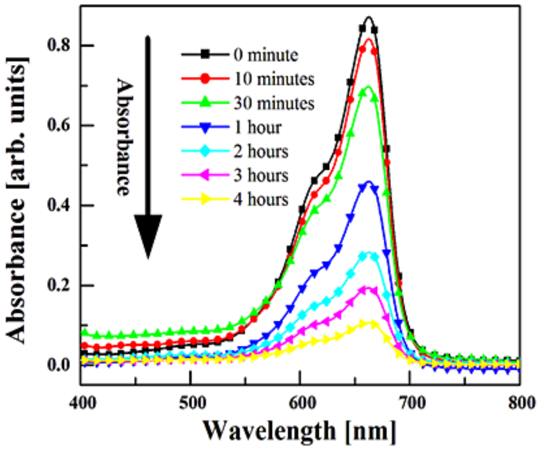

Fig. 6: UV-Visible spectra showing Ag NP assisted degradation of MB at different interval of time

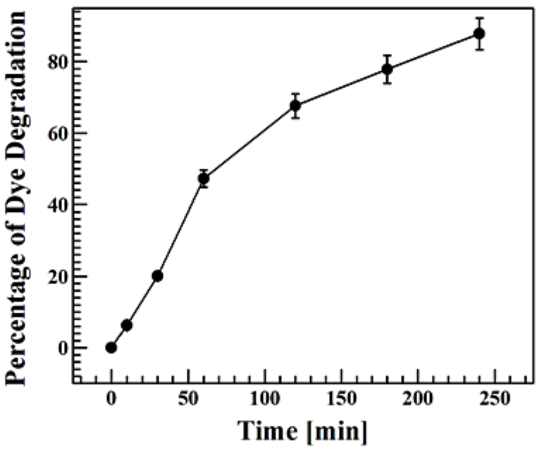

Fig. 7: Percentage of MB dye degradation with time. Filled circles are experimental data point

By absorbing the solar photons, excitation of surface plasmon electrons of Ag nanoparticles occurs. These excited electrons get absorbed by the dissolved oxygen molecules in the medium and transform them into superoxide oxygen radicals (•O2-) which is a very strong oxidizing agent capable to decompose the MB dye and degrade it.[34] This explains how Ag NPs degrade MB dye under solar light irradiation.

Conclusion

Here we have successfully synthesized silver nanoparticle at room temperature by using aqueous extract of Neem leaf and silver nitrate solution by green synthesis approach. No extra *chem*ical other than silver nitrate has been used here and hence it is eco-friendly and sustainable. Here the different biocompounds present in extract of Neem leaf serves reducing as well as capping agent. The formations of Ag nanoparticle was primarily confirmed through the colour change of the aqueous solution of silver nitrate and experimentally confirmed by optical absorption spectrum showing a broad absorption peaks at ~420 nm. The size of the particle was estimated by the image obtained by transmission electron microscope and found to be in the nanometer (10^{-9} m) scale. All the experimental findings are in line with the others' observational results and our previous work. The synthesized Ag nanoparticles are well crystalline and pure crystal of Ag as no other peak apart from the characteristic peaks is observed in XRD spectra. Finally it is to be concluded that, the biosynthesized Ag nanoparticles can be used in waste water treatment, textile industry or elsewhere as a photocatalytic agent for dye degradation in order to reduce toxic effects of synthetic dyes that pollutes the environment.

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Conflict of Interest

The author declares no conflict of interest.

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