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Green Biosynthesis of Silver Nanoparticles Using 'Polygonum *Hydropiper'* And Study Its Catalytic Degradation of Methylene Blue

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Abstract

The green synthesis of silver nanoparticles with the small size and high stability paved the way to improve and protect the environment by decreasing the use of toxic chemicals and eliminating biological risks in biomedical applications. Plant mediated synthesis of silver nanoparticles is gaining more importance owing its simplicity, rapid rate of synthesis of nanoparticles and eco-friendliness. In this study, focus on biosynthesis of silver nanoparticles using *Polygonum hydropiper* extract and its catalytic degradation of hazardous dye, methylene blue has been highlighted. The rapid reduction of silver (Ag) ions was monitored using UV-Visible spectrophotometer and showed formation of silver nanoparticles within less than one hour with maximum absorption of silver nanoparticles at 430 nm. The major functional groups present in the synthesis responsible for the formation of silver nanoparticles. It was identified by using Fourier Transform Infrared spectrophotometer (FTIR). Field Electron Scanning Microscope (FESEM) was used to characterise the nanoparticles synthesized using *P.hydropiper*. The morphology of silver nanoparticles was predominantly spherical and aggregated into irregular structure with average diameter of 60 nm. In addition, this report emphasizes the effect of the silver nanoparticles on the degradation rate of hazardous dyes by sodium borohydride ($NaBH_4$). The efficiency of silver nanoparticles as a promising candidate for the catalysis of organic dyes by $NaBH_4$ through the electron transfer process is established in the present study.

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*Keywords:*Nanosilver; Biosynthesis; *polygonum hydropiper*

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1. Introduction

In the last decade, the biosynthesis of nanoparticles, as a representative intersection of nanotechnology and biotechnology, has increasing attention due to the growing need to develop environmentally benign technologies in material synthesis. Although many synthetic technologies in material synthesis are well documented the search for suitable biomaterials for the biosynthesis of nanoparticles continues among researchers worldwide. Silver nanoparticles (AgNPs) are important materials that have been studied extensively. Such nanoscale materials possess unique electrical, optical as well as biological properties and are thus applied in catalysis, biosensing, imaging, drug delivery, nanodevice fabrication and medicine[17]. The metal nanoparticles have been synthesized using a variety of methods, including chemical and physical methods. Although nanoparticles can be made using various physicochemical methods, these methods are quite expensive and potentially dangerous to the environment. Other than, chemical methods employ toxic chemicals as reducing agents, organic solvents, or non biodegradable stabilizing agents and therefore potentially dangerous to the environment and biological systems. Thus, this will limit their applications. Use of biological organisms such as microorganisms and plant extracts could be an alternative to chemical and physical methods in an eco-friendly manner and green synthesis[7]. Moreover, the use of plant biomass and extracts for synthesis of nanoparticles is potentially advantageous over microorganisms due to several factors such as simple handling procedures, readily scalability and preclusion of cell culture maintenance. Furthermore, the plant biomass and extract can be obtained easily in due to availability and the abundance of plants that can be found in Malaysia. However, the selection of plant material is very critical in obtaining the best reducing agents in order to produce excellent size and shape of nanoparticles[3]. According to[10], biogenic synthesis is not only reduced environmental impact, but also can produce large quantities of nanoparticles that are free of contamination and have a well-defined size and morphology. Biosynthetic routes can actually provide nanoparticles of a better defined size and morphology than some of the physicochemical methods of production[15]. Due to their amenability to biological functionalization, the biological nanoparticles are finding important applications in the field of medicine. The antimicrobial potential of metal based nanoparticles has led to its incorporation in consumer, health-related and industrial products.Plant contains a complex network of metabolites and enzyme that can be manipulated to synthesize naoparticles. The main chemical constituents of these plants are flavonoids, flavonoids glycosides and phenylpropanoid glycosides. The presence of various chemical compounds in plant such as polyphenols, flavonoids, sterols, triterpenes, reducing sugar like glucose and fructose, and protein could help produce metallic nanoparticles.To achieve that, ‘kesum’ or *polygonum hydropiper*, which is a local herbaceous plant of the family *polygonaceae* will be selected as a medium for the biosynthesis nanoparticles. *Polygonum hydropiper* is a plant of the family *polygonaceae* It grows in damp places and shallow water. It is cosmopolitan plant, found in Australia, New Zealand, temperate Asia, Europe, and North America. It has some use as a spice because of its pungent flavour. *Polygonum hydropiper* has several active ingredients. Two bicyclic sesquiteroenoids are present, polygodial (tadeonal, an unsaturated dialdehyde with a drimane backbone) and waburganal, which has been found responsible for the pungent taste (hence its edibility). This plant is reported exhibit antioxidant activity that is one of the most main criteria in the biosynthesis of metal nanoparticles[14].The plant contains an essential oil (0.5%) which consists of monoterpenoids and sesquiterpenoids: α-pinene, β-pinene, 1,4-cineol, fenchone, α-humulene, β-ceryophyllene, trans-β-bergamotene.carboxylic acids (cinnamic,valeric and caproic acid) and their esters were present in traces. The composition depends strongly on genetic factors.Traditionally, this plant is used as a haemostatic, antimicrobial, anthelmintic and anti cancer agent[9]. Thus, these results are very encouraging and indicate that this herb should be studied more extensively to confirm this result and reveal other potential therapeutic effects

2 .Method & Characterization

The collected *Polygonum hydropiper* was washed thoroughly with distilled water. The dried leaves were powdered to fine particles using mixer grinder. For the preparation of aqueous leaf extract, 10g of leaf *Polygonum hydropiper* powder were dissolved in 100 ml of deionized water followed by boiling 60 ◦C for 10 minute. Leaf extract was then left in room temperature for 25 hours until further use. Finally, it was filtered through Whatman no.1 filter paper to obtain the pure leaf sample extract. The filtrate thus obtained were used as plant extract. For the

synthesis of AgNPs to occur, 90 ml of 0.01M Silver nitrate solution was mixed with 10 ml of plant extract by drop wise. For catalytic study,the mixture was heated gradually at 60–90 ◦C for 10 minute using water bath with the constant stirring. 1 ml of 0.1 M sodium borohydride, $NaBH_4$ solution was added to 1ml of 0.001 M methylene blue (MB). The solution was then made up to 10 ml using deionised water and vigorously stirred for 5 min. Then, 2 ml of silver colloid were added to solutions and stirred for five more minutes. The degradation of dyes was indicated by the decolourisation of the solution. For catalyzed reaction, the colour changes was observed for every two minutes and for uncatalyzed reaction, the colour changes was observed for every 10 minutes due to slow pace of degradation. Both of this reaction was allowed to occur under UV light with vigorously stirred[19].

3. Result & Discussion

3.1 Biosynthesis of silver nanoparticles using Polygonum Hydropiper extract.

The water soluble ingredients present in the extract were responsible for reduction of silver ions towards formation of silver nanoparticles. The formation of silver colloids was monitored by ultraviolet visible absorption spectra. As the leaf extracts were mixed with the aqueous solution of the silver ion complex, the colour of the reaction medium changed very rapidly from pale yellow to dark brown. The appearance of brown colour was due to excitation of surface Plasmon resonance, typical for silver nanoparticles (Vidhu e*t al*., 2005).

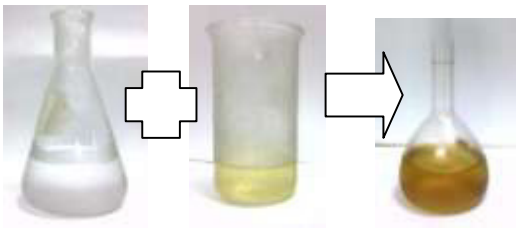

Fig. 1. Formation of AgNPs from *Polygonum Hydropiper* extract

3.2 UV-Visible spectral analysis

Metallic nanoparticles would show distinct absorption spectrum when suspended in aqueous suspension. Theoretically, colloidal silver nanoparticles possess optical spectrum with absorption peak, also known as the surface Plasmon resonance (SPR) lies in the range 400-460 nm. The appearance of a pale-yellowish to dark brown colour in the reaction flask was the indication of silver nanoparticles formation. Bioreduction of aqueous Ag^+ ions can easily be followed by UV-Vis spectrophotometer and one of the most important features in optical absorbance spectra of metal nanoparticles is surface Plasmon band, which is due to collective electron oscillation around the surface mode of the particles[1]. The colour intensity increased as a function of time due to reduction of silver ions. Thus, the verification for the silver nanoparticles formation was monitored by UV-Vis spectral analysis as shown in Fig. 2.

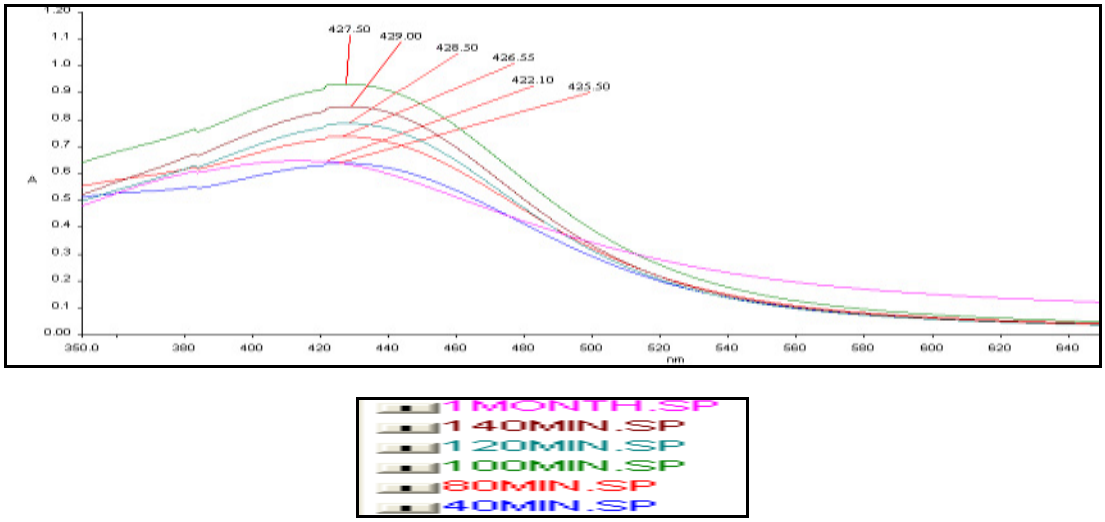

Fig. 2. UV-Visible spectra

Fig. 2 showed the UV-Visible spectra that were recorded at different time intervals for monitoring the reaction where the time interval is in the range of twenty minutes each. The appearance of the surface Plasmon resonance band (SPR) increased in intensity with time. The SPR results in unusually strong scattering and absorption properties. Due to the unique optical properties of silver nanoparticles, a great deal of information about the physical state can be obtained by analyzing the spectra. As the diameter increased, the peak Plasmon resonance shifts to longer wavelengths and broadens. The band wavelength, the band width, and the effect of secondary resonance yield a unique spectral fingerprint for plasmonic nanoparticles with a specific size and shape. Thus, this is proved that the surface Plasmon resonance bands are influenced by size, shape, morphology, composition and dielectric environment of the prepared nanoparticles[11]. From the result, the reduction of silver ions and the formation of silver nanoparticles were occurred less than 30 minutes making it one of the fastest bio reducing methods to produce AgNPs[12]. The absorption spectra of silver nanoparticles formed in the reaction media has narrow absorbance peak at 430 nm. According to Mie's theory, small spherical or quasi-spherical nanocrystals exhibit a single SPR band, where anisotropic particles show two or three bands, depending on their shape. This value was in good agreement with the reported literature for AgNPs. The broadening of peak indicated that the particles are spherical-polydispersed and further confirm with FESEM. The surface Plasmon band in the AgNPs solution remains close to 430 nm throughout the reaction period indicating that the particles are dispersed in the aqueous solution, with no evidence for aggregation. This is the ability of UV-Visible spectroscopy that can be used as a simple and reliable method for monitoring the stability of nanoparticle solutions. As a particles destabilize, the original peak intensity will decrease due to the depletion of stable nanoparticles and often the peak will become broaden .Thus, it was observed that the nanoparticles solution was stable for more than one month's with little signs of aggregation. At the same time, from the shape of the absorption peak we can also acquire information on the changes of the size distribution. The position of the peak directly depends on the size of nanoparticles[17]. As we know, when the solution system was quite spherical-polydispersed (narrow size distribution) the peak shape symmetric and the value of the FWHM was medium in value. When the system was polydisperse, the peak shape was asymmetric[4]. The width at half maximum can be useful to find size distribution of the particles in a solution. The broader the peak, the broader is the size distribution of the particles. From the finding, the FWHM, was typically around 80-100 nm. Both the absorption peak and the FWHM were in accordance with the normal pure silver nanoparticles. The increase in intensity could be due to increasing number of nanoparticles formed as a result of reduction of silver ions present in the aqueous solution.

The silver nanoparticles that produced from *Polygonum hydropiper* are comparable with the previous research of AgNPs produced from *Citrus Limon*[13]. The absorbance peak was shifting towards larger wavelength which is 580 nm. Therefore, different plant extract may gives different absorbance peak value due to their differences in

characteristics silver surface Plasmon.

3.3 Fourier Transform-Infrared spectral analysis

The green synthesis of silver nanoparticles by employing *Polygonum hydropiper* leaf extract was further investigated using Fourier Transform Infrared spectroscopy (FTIR). Based on Fig.3, the information regarding the potential bio molecules in *Polygonum hydropiper* leaf extract which is responsible for reducing and capping the bio reduced AgNPs can be obtained.

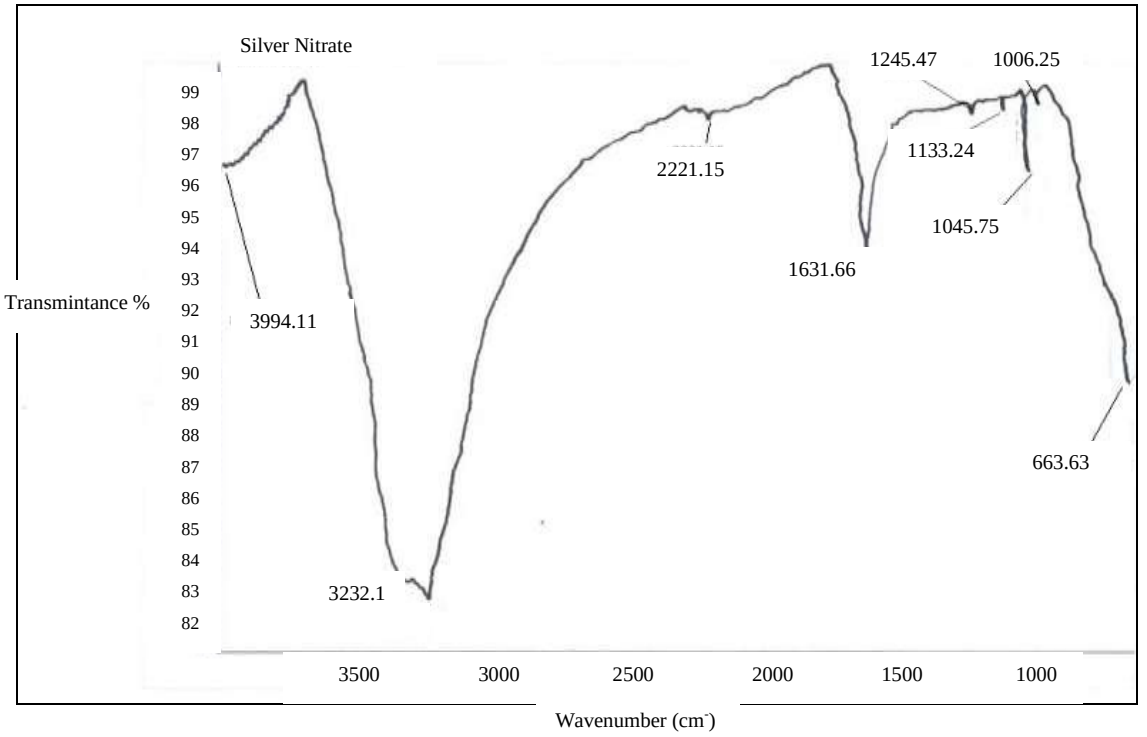

Fig. 3. Fourier Transform-Infrared spectrum

Fig. 3 showed intense FT-IR bands observed at 3232.14 and 1631.66 cm^{-1} which indicate the presence of molecular functional groups that are responsible for the reduction of silver ions. The strong and broad peaks at 3232.13 cm^{-1} unveil the presence of phenolic compounds with hydroxyl group (663.63 cm^{-1}). This also might be ascribed to the hydrogen-bonded O-H stretch. Other than that, functional group of C=C stretching which is alkene existed in the silver nanoparticles based on the observable strong peak at 1631.66 cm^{-1}.In addition, this band might designated to the vibrational frequencies corresponding to amide protein. The absorption bands at the 2700 to 1850 cm^{-1} region usually come only from triple bonds and other limited types of functional groups. Stretching band can be found in silver nanoparticles which are corresponding to aldehyde stretch groups. Fourier transform infrared spectroscopy analysis of the silver nanoparticles showed absorption peaks of reduced silver at 1245.47 $cm^{-1}$and 1133.24 cm^{-1}. The C-O single bond can vary anywhere between 1000 cm^{-1} and 1300 cm^{-1} depending what sort of compound they are in. Biological components are known to interact with metal salts via these functional groups and mediate their reduction to nanoparticles[6]. The results also entail that the phenolic compounds and protein may play a vital role in the formation of AgNPs. However, several reports have suggested that the formation of AgNPs might be due to the presence of proteins, free amine, carbonyl, and phenolic groups. This functional group may encapsulate the surface of silver ions by stabilizing the nanoparticles as capping agents. But the exact mechanism involved in the formation of AgNPs is still a debated[13].

3.4 FESEM analysis of silver nanoparticles.

The size and shape of the silver nanoparticles were further characterized by FESEM analysis. The FESEM images show individual silver nanoparticles as well as a number of aggregates. Fig. 4 and 5 clearly shows the presence of the synthesized silver nanoparticles with magnification x25000 and x50000. Mostly nanoparticles were spherical, oval in shape and mostly aggregated and few individual particles are present. It is known that the shape of metal nanoparticles can considerably change their optical and electronic properties[16]. Moreover, there is a point of view for nanoparticle to congregate or assemble each other at higher intensification by microscope. The diameter range for each nanoparticles present in the SEM images is in the range of 45 to 70 nm with the average diameter 60 nm in size. The water soluble heterocyclic compounds were mainly responsible for the reduction of silver ions or chloroaurate ions to metallic silver[16]

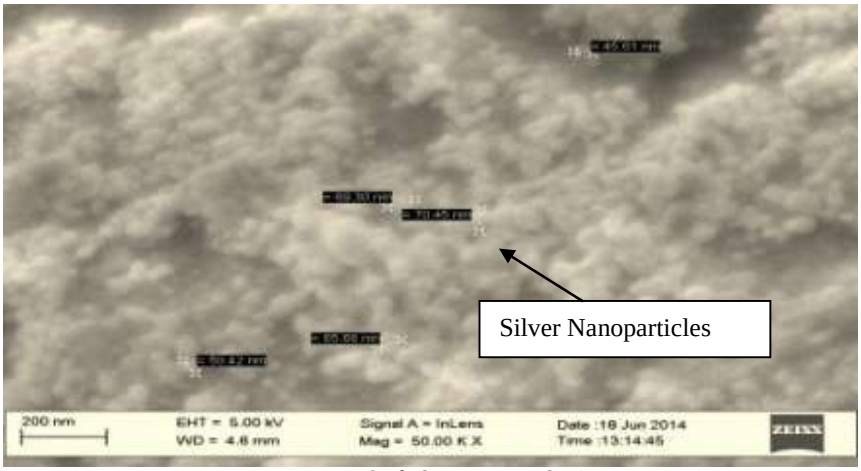

Fig. 4. FESEM micrograph of silver nanoparticles (Mag = 50 K x)

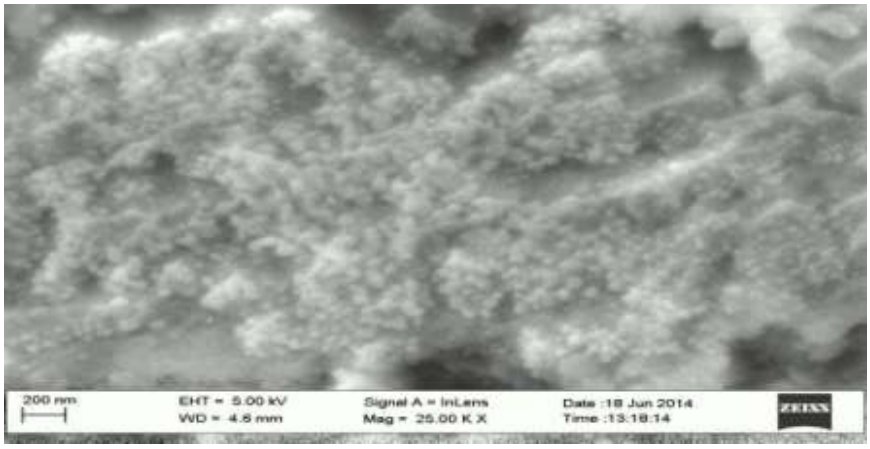

Fig. 5. FESEM micrograph of silver nanoparticles (Mag = 25 K x)

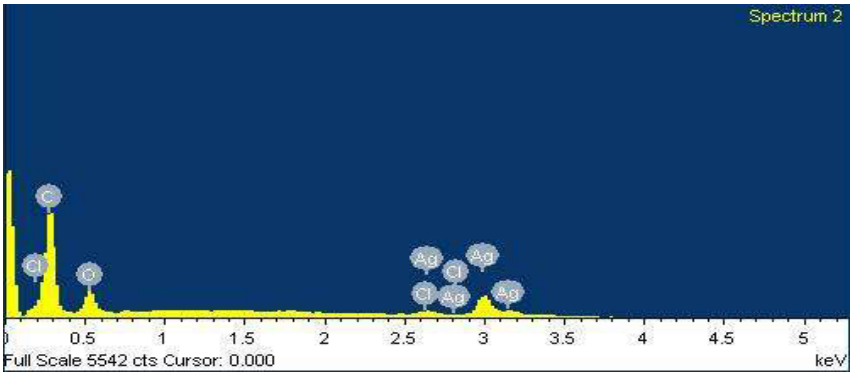

Fig. 6. Energy Dispersive Spectroscopy spectrums of AgNPs

Table 1.Elemental components existed in sample of silver nanoparticles

Element	Weight %	Atomic %
Carbon	14.04	51.13
Oxygen	5.15	14.07
Chlorine	2.47	3.04
Silver	78.34	31.76
Totals	100.00	

Fig. 6 shows the EDX spectra of AgNPs synthesized at room temperature to further confirmed the presence of silver atoms in silver nanoparticles**.** The presence of the elemental silver can be observed in the graph obtained from EDX analysis. It is clear that AgNPs reduced by *Polygonum hydropiper* have the weight percentage of silver of 78.34%. This indicates the reduction of silver ions into elements of silver.The optical absorption peak was observed at 2.6, 2.8, 3.0 and 3.2 keV, which is typical for the absorption of silver nanocrystallites due to SPR. Thus, this proved that the elements existed was a silver. In an earlier study, individual spherical silver nanoparticles synthesized by using *Trianthemadecandra* showed absorption peaks in the range 2.8- 3.8 keV which is same with this result that using *Polygonum hydropiper* as reducing agents. The EDX analysis also shows the weak signals of carbon, oxygen and chlorine. The presence oxygen's peak along with the Ag signals, suggest that the AgNPs are capped by phytoconstituents through oxygen atoms[19]. Another weak signal could have arisen from the bio molecules present in the plant extract. It has been reported that nanoparticles synthesized using plant extracts are surrounded by a thin layer of some capping organic material from the leaf thus stable in solution up to six months after synthesis[1].

3.5 Catalytic activity of AgNPs on reduction of methylene blue (MB).

One of the important applications of metal nanoparticles is to catalyze some reactions that are otherwise unachievable. It is well-known that the catalytic activity of nanoparticles was strongly dependent on its composition, size and shape. Typically, a bigger surface-to-volume ratio is given to show a higher catalytic activity[5].It is a well known fact that AgNPs and their composites show greater catalytic activity in the area of dye reduction and removal. The use of MB, a heterocyclic aromatic dye, in the textile has increased in the last few years. The silver nanoparticles thus prepared by the mentioned procedure were used as catalyst for the reduction of methylene blue by $NaBH_4$.The degradation's rate of MB's colour in the presence of $NaBH_4$ was observed in the presence and absence of silver nanoparticles as catalyst. Fig. **7** shows that the reduction of MB with ($NaBH_4$) in absence of silver nanoparticles (catalyst) at 20 °C under UV light with vigorously stirred occurs at an extremely slow rate without any differences in colour by observing using naked eyes. This result proves that, although after 80 minute of reaction between MB with strong reducing agent $NaBH_4$, there is no degradation of MB that can be seen. But on the addition of silver nanoparticles, degradation of the dye MB is greatly enhanced. The disappearance of blue colour of MB in solution (Figure **8**) was due to the reduction of methylene blue. The methylene blue solution turns into completely colourless (LCB) solution within less than 15 minute under UV light with vigorously stirred. Similar results show by using the biosynthesized AgNPs using *Trigonella foenum-graecum* seeds extract. The plot of relative absorption

intensity with wavelength in a regular interval of time (1 minute) reveals that the complete reduction of MB to leucomethylene blue (LMB) was accomplished in less than 20 min in the presence of silver nanoparticles[19]. To act as an effective catalyst, the redox potential of AgNPs needs to be found between the redox potential of donor ($NaBH_4$) and the acceptor (MB) system (Mallick *et al*., 2012). This result proves that AgNPs can act as an effective catalyst in the reduction of MB by $NaBH_4$into photo chemically inactive LCB.Usually, the catalytic activity is positively related with the surface area of catalyst. It is well-known that the size of metal nanoparticles plays an important role in catalytic reduction. When the size of AgNPs decreases, there is an increase in the number of low coordinated Ag atoms which promote the adsorption of the reactants MB on the catalyst surface and facilitates the reduction. Similar results also were reported the silver nanoaprticles from using *Terminalia chebula* fruit extract and their catalytic activity on reduction of MB[19].

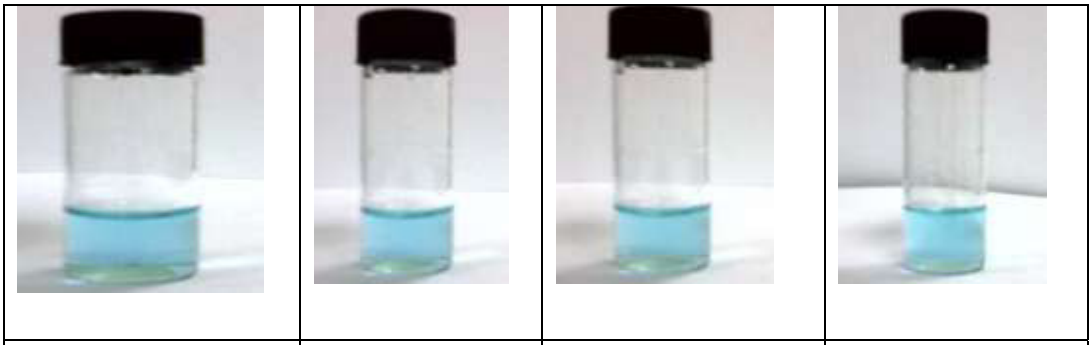

Fig. 7. Uncatalyzed reactions (In the absence of AgNPs)

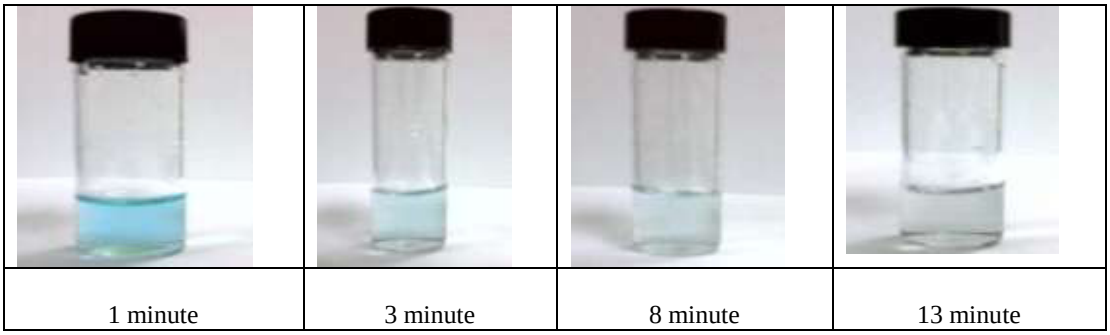

Fig. 8.Catalyzed reaction (In the present of AgNPs)

4. Conclusions

This study reports successfully biosynthesis of silver nanoparticles using *Polygonum hydropiper* as a novel reducing and stabilizing agents of silver ions that offers a valuable contribution in the area of green synthesis and nanotechnology. This biological synthesis was shown to be rapid and produce particles of predominantly spherical and aggregated into irregular structure with average diameter of 60 nm in size. The catalytic effectiveness of silver nanoparticles monitored for reduction of methylene blue by sodium borohydride show very fast reaction that change the methylene blue into leucomethylene blue (colourless) with the present of AgNPs as catalyst. Sodium borohydride being strong reducing agents is not able to reduce methylene blue in absence of catalyst, indicating the catalytic efficiency of silver nanoparticle (AgNPs).

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