Green Synthesis of Silver Nanoparticles Using *Citrus Sinesis* (ORANGE) Peels And Its Application

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Abstract- *Over past few years nanotechnology field has been an important part of research. In this study, eco-friendly method was used for synthesis of silver nanoparticles using citrus fruits. One of the widely-studied properties of silver nanoparticles is Surface Plasmon Resonance. Silver nanoparticles have application in dye degradation. As organic dyes which are used in textile, medicine or in any industry has hazardous effect in environment, it is necessary to degrade this dye using silver nanoparticles. Citrus sinesis is used for synthesis of silver nanoparticles which itself act as capping and reducing agent, thus there is no need of any chemical reducing agent. The silver nanoparticles were formed within 15minutes and appeared brown color solution. UV-visible spectroscopy was used for characterization and maximum peak of C. sinesis was found to be 440nm. This method is one step, rapid and safe as compared to the other methods. The synthesized silver nanoparticles were used to degrade methylene blue and saffranin dye by photocatalytic activity.*

Keywords- Silver nanoparticles, Eco friendly, C. sinesis, UV-visible spectroscopy, Dye degradation.

I. INTRODUCTION

Nanotechnology is the field that deals with synthesis of nanoparticles which range from 1nm to 100nm. They possess different sizes and shape, such as triangular, spherical, irregular, etc **[7]**. In recent years, nanoparticles synthesis has received considerable attention due to their unique properties and potential applications **[4 and 9]**. There are various nanoparticles silver, gold copper, etc. but out of these silver nanoparticles (AgNPs) have gained much importance due to its unique properties. One of the widely-studied properties of silver nanoparticles is Surface Plasmon Resonance that is the strong interaction of the silver nanoparticles with light occurs because the conduction electrons on the metal surface undergo a collective oscillation when excited by light at specific wavelength **[8]**. Silver nanoparticles possess very high aspect ratio apart from of their synthesis process which determines surface related properties such as solubility and stability. They also possess optical and electrical property. It has various applications in field of engineering, medicine and chemistry.

In conventional methods, silver nanoparticles were synthesized using toxic reducing agents such as sodium borohydride, trisodium citrate and hydrazine. To solve this problem, nowadays researchers have focused on green synthesis method. This method is environment friendly where natural, safe and low cost reducing agents are used. Silver nanoparticles are formed due to reduction of silver ions into neutral silver atoms. Biosynthesis of silver nanoparticles using citrus fruits is bottom up approach where there is reduction involved of silver ions.

In the present study, peels of *Citrus sinesis* (orange peels) were used which are rich source of flavones, polymethoxylated flavones and vitamin C. This peels act as capping and reducing agent and help in synthesis of silver nanoparticles. The use of environmentally benign materials for the synthesis of nanoparticles offers numerous benefits in pharmaceutical and biomedical applications as toxic chemical substances are not employed in their synthesis **[6]**. Characterization was also carried out using UV-visible spectroscopy for confirmation of silver nanoparticles.

Silver nanoparticles have application in industry for degradation of dyes. The organic dyes which are used in textile, medicine or in any industry have hazardous effect in environment. A major threat is industries use this dyes in high amount and are not degradable by conventional methods. These dyes are released in waste water which causes pollution and affect humans and environment. The important criteria are these dyes should be stable in light while washing **[2]**. Also, the accumulation of dyes in water bodies lead to eutrophication that is it reduces reoxygenation capacity and affects the aquatic organisms by hindering infiltration of sunlight **[2]**. Most of industrial dyes are resistant to microbial attacks and degradation by conventional methods like adsorption, ultrafiltration and electrical methods. Therefore, silver nanoparticles are used to degrade these dyes as they have advantage over other methods such as rapid oxidation and also the size, shape and surface area has made the silver nanoparticles high photocatalytic activities. These nanoparticles effectively degrade the dye.

II. MATERIALS

1. *Citrus sinesis* (Orange peel) from local market
2. Methylene Blue dye (MB)
3. Saffranin dye (S)
4. Silver Nitrate from Lobachemie

III. METHODS

- **Preparation of *Citrus* fruit extract-**

A) *Citrus sinesis* extract-

Fresh *C. sinesis* (orange) fruit was brought from local market. The peels were removed, washed with distilled water and then allowed to dry partially. The peels were cut into small pieces. Weigh about 4g of peels and add 40mL distilled water in 250mL of beaker. Boil the extract for 2 minutes. Then filter the extract using Whatmann filter paper. Collect the filtrate and stored at 4℃ for further use **[1]**.

- **Preparation of 1mM Silver Nitrate-**

Silver nitrate was brought from Lobachemie. Weigh 0.0169gm of silver nitrate and dissolve in 100mL of distilled water in amber coloured bottle.

- **Synthesis of Silver Nanoparticles-**

40mL of 1mM of silver nitrate solution was heated till it gets boiled. Then, 3mL of orange peel extract was added till pale yellow is obtained. Incubated in dark at room temperature.

- **Characterization of Silver Nanoparticles-**

Then synthesis of silver nanoparticles was checked in UV-Visible spectroscopy at the wavelength of 300-700nm.

- **Dye Degradation-**

5mg of methylene blue dye was dissolved in 100mL of distilled water. 5mL of synthesized silver nanoparticles was added to this dye solution. The mixture is kept on shaker in dark for 45minutes. Similarly saffranin dye degradation was carried out. The dye solution (without silver nanoparticles) is kept as control. After incubation, the solution is exposed to the sunlight. Zero hour reading is taken in colorimeter at wavelength from 400-700nm. Similarly at every two hours the aliquot is taken and filtered through Whatmann filter paper and reading was taken.

IV. RESULTS AND DISCUSSION

1) Synthesis of silver nanoparticles-

The colour of extract was yellow in colour. After the addition of extract into silver nitrate solution the colour was changed to colourless. After incubation, the colour was changed from colourless to brown within 15minutes (fig no.1). This indicates that the silver nanoparticles were synthesized using both the extracts.

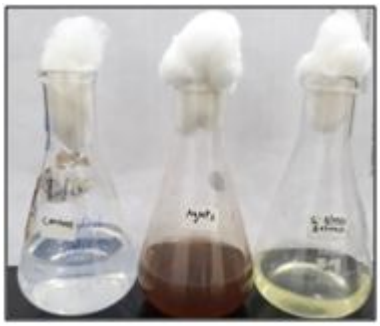

Fig no.1-Formation of Silver Nanoparticles (Brown Colouration)

2) UV-Visible Spectroscopy-

Reduction of Ag^{+} to Ag^{0} was confirmed using UV-Visible spectroscopy at 300-700nm of wavelength. The maximum peak of absorption of silver nanoparticles using *C. sinesis* and was observed at 440nm (fig no.2). The silver nanoparticles have free electrons which give rise to surface plasmon resonance band. This reduction of silver ions was due to surface plasmon resonance and this SPR is formed due to particle shape and size **[2]**. UV-visible spectroscopy is useful technique for confirmation of synthesis of silver nanoparticles. The formation was within 2hrs of incubation in dark due to orange peel which itself act as s capping and reducing agent.

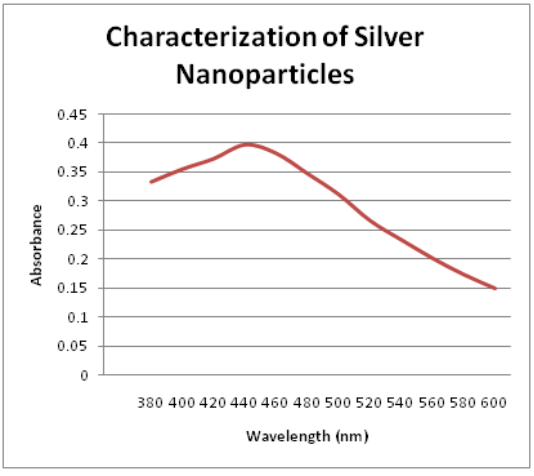

Fig no.2-Graph of Characterization of Silver Nanoparticles

3) Dye Degradation-

Methylene blue dye is an aromatic cationic dye which is widely used in textile industries. This dyes causes eye and skin irritation, gastrointestinal tract and other problems **[5 and 7]**. After exposure to sunlight, it was observed that within 30 minutes the colour of the started changing. First it was visually observed that the dye colour changes from blue to light blue and then to colourless after 6 hours of incubation in sunlight (fig no.3). This results were confirmed by absorption band using colorimeter at 400-700nm. The absorption peak of the methylene blue dye was observed to be at 420nm (fig no.4). The degradation of this dye was confirmed by gradual decrease in peak intensity with extension of exposure time.

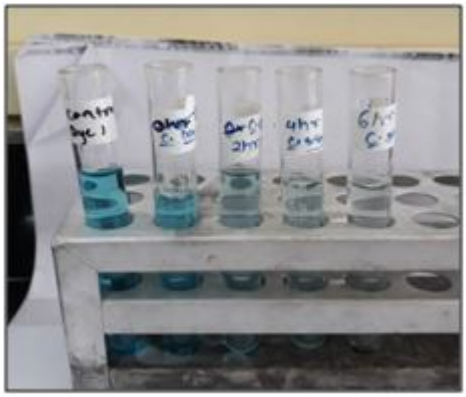

Fig no.3- Degradation of Methylene Blue

Wavelength (nm)	Absorbance at different time intervals			
	0hr	2hrs	4hrs	6hrs
Blank	-	-	-	-
400	0.12	0.10	0.05	0.03
420	0.15	0.14	0.09	0.06
470	0.09	0.06	0.03	-
500	0.14	0.09	0.09	0.09
530	0.08	0.08	0.07	0.06
620	0.08	0.06	0.01	-
660	0.03	0.02	0.01	-
700	0.03	0.01	0.01	-

Fig no. 4-Readings of Methylene Blue Degradation

Similarly, saffranin dye was causes environmental problems. This dye also starts degrading within 30 minutes by change in colour from pink to light pink. The absorption peak was observed at 660nm (fig no. 6) and degradation was confirmed by gradual decrease in peak intensity. Researchers revealed that the degradation of dye using silver nanoparticles by an action of photocatalytic depends on structure, size, morphology and crystalline nature of the particles **[2, 10]**. At the time of degradation the catalysis occurs on surface region of silver, making surface area increase and thereby improves silver as efficient catalyst. Thus it acts as an efficient catalyst in all the above catalytic process **[3]**.

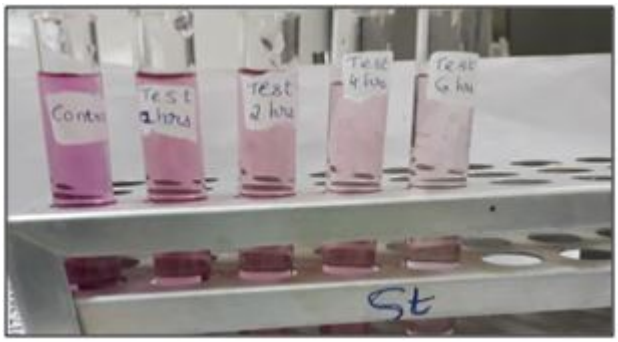

Fig no.5- Degradation of Saffranin Dye.

Wavelength (nm)	Absorbance at different time intervals			
	0hr	2hrs	4hrs	6hrs
Blank	-	-	-	-
400	0.14	0.05	0.01	-
420	0.08	0.03	0.03	-
470	0.06	0.01	0.01	-
500	0.05	0.02	0.01	-
530	0.06	0.06	0.03	-
620	0.13	0.05	0.04	0.04
660	0.14	0.12	0.08	0.06
700	0.13	0.03	0.03	0.01

Fig no.6- Readings of Saffranin Dye Degradation

V. CONCLUSION

For future technology, this green synthesis method should be employed to overcome the conventional methods. Silver nanoparticles were synthesized using *Citrus sinesis* peels by green synthesis method. This method is rapid, cost effective, non-toxic and eco friendly. Also these nanoparticles have high degradation activity and act as an efficient catalyst. The synthesized silver nanoparticles degrade the methylene blue and saffranin dye efficiently by photocatalytic activity. This approach helps to reduce the environmental and human health problems.

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