Photocatalytic Dye Degradation Using Nanoparticles From Fruit Waste

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Abstract- *Bio-waste as a source of synthesis Silver Nanoparticals (AgNPs) opens a new path along with antimicrobial and photocatalytic degradation of azo dyes such as Methylene blue and Congo red. In this study, we have synthesized Silver Nanoparticles using multiple fruit peel waste extract (pomegranate, papaya, banana and pineapple). This appears extremely fast, cost efficient, eco-friendly method. The primarily nanoparticles formation has been confirmed by the color change pale yellow to brown and that indicates reduction of silver ions to silver nanoparticles. The formation of AgNPs was confirmed by its absorbance peak observed at 430nm in UV-Visible spectrum and partical size analysis by NANOPHOX (NX0088) and found to be 7.7nm. The photocatalytic activity of the synthesized silver nanoparticles was examined by degradation of Methylene blue and Congo red dye under sunlight irradiation. Green synthesized silver nanoparticles were effectively degrade the dye at 5-6 h of exposure time. (AgNPs) can be used in textile industries to treat polluted water containing non-degradable dyes and effective against disease causing micro-organisms.*

Keywords- Silver Nanoparticles, biosynthesis, Partical size, Antimicrobial, Organic dyes, Photocatalytic degradation.

I. INTRODUCTION

Dyes which cause pollution to the water bodies are organic and widely used in textile, plastic, medicine and many other industries, while the hazardous effects of organic dyes in waste water have been a major concern and now a major threat in the environment due to the substantial pollution problems caused by them. These industries exhausted large quantity of high content color effluents, which are generally more toxic and resistant to destruction by conventional methods. A necessary criterion in the use of these dyes is that they must be highly accumulated in water .and stable in light during washing. The accumulation of these dyes in the water bodies causes hazardous effects on aquatic flora and fauna, eutrophication, reduces the re-oxygenation capacity and makes severe damage to the aquatic organisms by hindering the infiltration of sunlight[1].An alternative type of catalysts for photo-degradation of organic dyes is nanoparticles of some transition metals such as silver. The size, shape, large surface area to volume ratio and mass dependent reactivity has made metal nanoparticles high photocatalytic activities[2].MB, an aromatic cationic dye, is widely deployed in textile industries for various purposes. Accumulation of MB in water bodies contaminate waters which might lead to eye irritation, gastrointestinal tract and skin irritation [3].CR, a secondary diazo anionic dye, is most often used dye in industries,contain carcinogenic metabolite, which are hazardous to leaving one. Benzidine of CR is known to cause bladder cancer among humans. It is also studied that the effluents with CR are highly coloured and possess high chemical oxygen demand along with high amount of dissolved solids[4].

The novel properties of nanoparticles are widely deployed for various applications in medicine, cosmetics, biomedical devices and environmental remediation[5].The properties and function of the nanoparticles are size and shape dependent. Consequently, for a better antibacterial and catalytic activity a specific control over the shape and size of the nanoparticles is prerequisite, which could be achieved by employing different synthesis methods, reducing agents and stabilizer[6,7].Green synthesis approach is eco-friendly, cost effective and provides single step synthesis of nanoparticles[8,9]. In this study showed use of Silver biosynthesized using different fruit peels in photocatalytic degradation of Congo red and Methylene blue .

II. MATERIALS & METHODS

The chemicals silver nitrate (SRL chemicals) extra pure AR ACS ExiPLus were used for synthesis of Silver Nanoparticales Fruit Peels,orange *(Citrus aurantium*),banana (*Musa acuminata*), pineapple *(Ananas comosus),* papaya *(Carica papaya)* were collected from local areas fruit Juice Centre and were surface washed using double distilled water. Methylene blue and Congo red (Fisher Scientific) were used.

2.1 Biosynthesis and Characterization of Silver Nanoparticles

The aqueous extract fruit peels was prepared by boiling 5g of each samples in fruit waste peels mention above, in 100ml of distilled water at 100°C for 10min. The extract was further filtered through Whatman filter paper No. 1and stored at 4°C for further use. 5mM Silver Nitrate Solution was prepared using double distilled water, AgNPs were synthesized by addition of the 10 ml aqueous fruit peels extract to the 90ml of silver nitrate solution in an Erlenmeyer flask. Synthesis of AgNPs were confirmed by color change and more analysis by UV-vis spectrophotometer , Particle size analyser and Zeta Potential.

2.2 Photocatalysis:

In Experimental set up,10ml of 5mM of AgNPs were added to employing 10 ml 0f Methylene blue (10mg l^{-1})and Congo red (100mg l^{-1})aqueous solution(kumara paper).. The suspension mixture's were kept on magnetic stirrer for 10 min in dark to bring the AgNPs to constant equilibrium in the mixture. Catalytic degradation reaction were conducted under sunlight. For 6-7 hours and centrifuge at 10,000rpm for 10min and OD was then measured at 300-650nm(CR) and 400-700(MB) to ensure photo detoxification of the dye[10,11].Respective dye solution10ml each were kept as control.

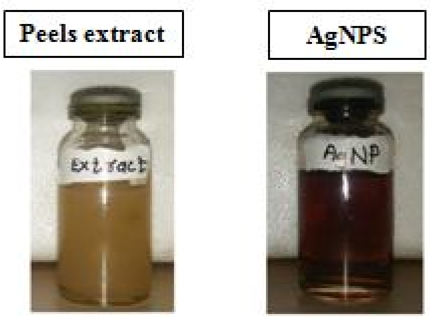


Figure1: Visual observation of AgNPs synthesis: (1)before addition of AgNO3,(2)after addition of AgNO3 and depicting synthesis of AgNPs as the colour turns to dark. brown in colour

III. RESULTS AND DISCUSSION

Generally, the reduction and stabilization of the AgNPs are aided by the phytochemicals and phenolics present in the plant extracts. These organics in fruit peels could probably aid in the synthesis of AgNPs. 10ml of extract was added dropwise to the 5Mm of Silver Nitrate solution. The AgNPs formation was indicated by the gradual colour change of the solution from light to dark brown **(figure1.)** confirmed the presence of AgNPs in the suspension.

3.1 UV – Spectrophotometer:

Silver nanoparticles appears dark brownishin color aqueous in medium. As different fruit waste extract were added in silver nitrate, the color of solution dark brown. and further confirmed by the UV–spectrophotometer recorded within range of 330nm –550nm. The maximum absorption peak for silver nanoparticles was found to be 439nm(**Figure2.**) .According to Mie's Theory only single surface plasmon resonance (SRP) band is expected in absorption spectra of spherical nanoparticles. SRP is caused due to collective oscillation of the conduction electrons of nanoparticles upon erradiation with visible light.(12) where the addition of aqueous fruit peel extract to 5mM aqueous AgNO3 solution started its color change due to the excitation of SPR in the production of silver nanoparticles (13,14). SPR is caused due to collective oscillations of the conduction electrons of nanoparticles upon irradiation with visible light (15). The SPR is highly influenced by shape and size of the nanoparticals.

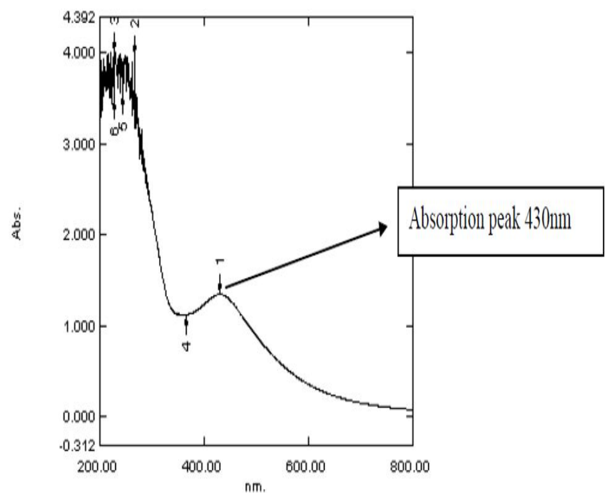


Figure 2: UV-Vis spectra of biosynthesized AgNPs recorded as a function of concentration of Silver Nanoparticals

DLS method:

Particle size determined by measuring the random changes in intensity of light scattered from a suspension or dispersion DLS method **(figure 3)**. This random motion is measured to calculate particle size. Particle size was analyzed by particle analyzer (NANOPHOX) which shows size of 7.7 nm.

solution of spherical particles in Brownian motion causes a Doppler shift when they are exposed against shining monochromatic light (laser). Such monochromatic light exposure hits the moving particle which results in changing the wavelength of the incoming light. Extent of this change in wavelength determines the size of the particle(16).

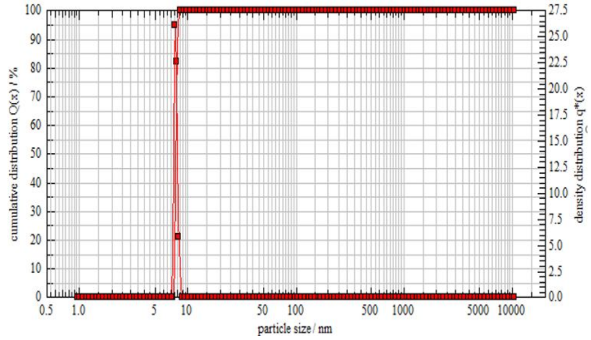
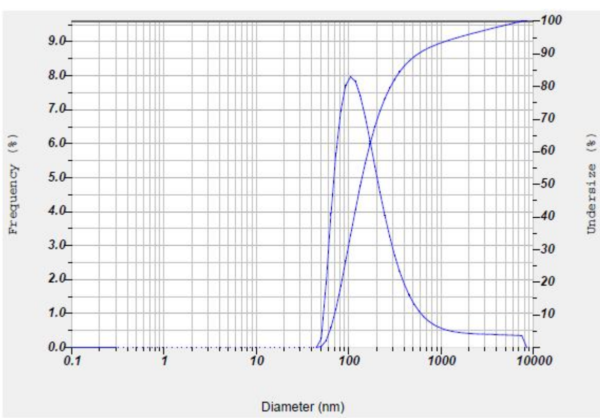


Figure 3.Partical size By DLS method

Zeta potential:-

The zeta potential of sample is most often used as indicator of dispersion stability**(figure4)**. Large zeta potentials predict a more stable dispersion. Liquid samples of the nanoparticles (5ml) were diluted with double distilled water (50 mL) using NaCl as suspending electrolyte solution (2 x10-2 M NaCl). The pH was then adjusted to the required value. The samples were shaken for 30 minutes. After shaking, the equilibrium pH was recorded and the zeta potential of the metallic particles was measured. A zeta potential was used to determine the surface potential of the Silver Nanoparticles. In each case, an average of three separate measurements was reported. The criteria of stability of AgNPs are measured when the values of zeta potential ranged from higher than +30 mV to lower than-30mV.



Photocatalytic activity:

Photocatalytic activity of the AgNPs was determined using detoxification of MB and CR under sunlight for a particular period(5-6) h of time. Initially, the catalytic degradation of the dyes in the presence of AgNPs was observed visually by the change in colour intensity. The intensity of the colour gradually decreased with time from dark blue/orange to light blue/yellow marking an effective photocatalytic degradation activity of AgNPs**(figure4).** Thereafter, the results were confirmed by obtaining absorption wavelength of the dye solution before and after treatment with AgNPs. The mechanism may depend on the ability of degraded compound to be absorbed on the surface of catalyst by consisting of free radical reaction intiated by UV light(17)

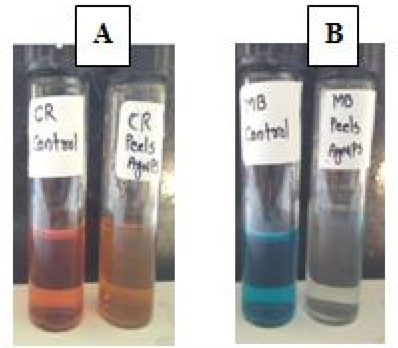


Figure 3.(A)Original Congo red solution Control and colour change Congo red(yellow) After 5-6 h, exposure of sunlight eradication with fruit peels AgNPs. Figure 4.(B)Original Methylene blue control to colour change.

Generally, the maximum absorption band of MB aqueous solution is observed at 700nm owing to the n-π* transition of the MB [18,19]. Whereas in present case, the MB solution was exposed for a period of 6h that showed significant decrease in the absorbance. The photocatalytic degradation of the dye was monitored using Spectrophotometer. The characteristic absorbance of CR is obtained around 650nm. The complete degradation of dye was observed within 20min from bright orange colour to light brick colour. Initial and final readings were recorded in term of concentration versus absorbance. **(Table1).** Final readings in all three sets of dye treatment were found significantly lower absorbance indicates degradation. The probable mechanism of degradation could be attributed to the SPR effect where the excited surface electrons might interact with the dissolved oxygen molecules and ultimately produce hydroxyl radicals while allowing Ag^+ ions to interact with the anionic dye [20,21]. Hence, it is evident that AgNPs synthesized from extract of fruits peels is highly potential photocatalytic agent for dye degradation in the presence of sunlight.

Table 1: Showing degradation of Congo red and Methylene blue dye. Initial and final reading in absorbance in spectrophotometer were taken with and without addition of AgNPs of Congo red and Methylene blue (Azo dyes) at300-650nm and 400-750nm respectively

Observation Table 1.	Absorbance(nm)					
	Congo red			Methylene blue		
	1	2	3	1	2	3
Initial absorbance Without AgNPs	0.14	0.14	0.14	0.19	0.19	0.19
Final absorbance AgNPs + Dye	0.11	0.12	0.11	0.09	0.10	0.00
Difference (Final-Initial)	0.3	0.2	0.3	0.10	0.09	0.19

IV. CONCLUSION

Degradation of dye by using waste like fruits peels nanoparticles synthesis by using eco-friendly and renewable molecules to get rid of hazards arising out of the use of chemical reducing agents and organic solvents.The biosynthesized AgNPs exhibits a very high degradation activity under visible light source. In the present research paper, we have demonstrated the synthesis of silver nanoparticles with extract of different fruit peels. The bioreduced AgNPs exhibited remarkable degradation properties in a reduction of organic dyes, (MB,CR) and show effective method to treat textile industry pollutant in form of non-degradable and carcinogenic dyes in economic way to environmental bioremediation protection

REFERENCES

[1] M.Faisal,M.A.Tariq,M.Muneer, "Photocatalysed degradation of two selected dyes in UV-irradiated aqueous suspensions of titania. Dyes Pigm", 233–239,2007.

[2] S.K.Ghosh,S.Kundu,M.Mandal,T.Pal, "Silver and gold nanocluster catalyzed reduction of methylene blue by arsine in a micellar medium, Langmuir", 8756–8760,2002.

[3] L.S.Oliveira,A.S.Franca,T.M.Alves and S.D.Rocha, "Journal of Hazardous Mate",2008.

[4] S.Maiti,S.Purakayastha and B.Ghosh, "Chem. Eng. Commun",2007.

[5] V.Vilas ,D.Philip and J.Mathew, " Spectrochim. Acta Part A: Mol. Biomol. Spectrosc",2004.

[6] S.Y.Yeo,H.J.Lee and S.H.Jeo,Journal of Material Science,2003.

[7] K.N.Thakkar,S.S.Mhatre and R.Y.Parikh , "Nanomedicine: Nanotechnology. Biol.Med",2010.

[8] V.A.Kumar,T.Uchida,T.Mizuki,Y.Nakajima,Y.Katsube,T .Hanajiri and T.Maekawa,A "dv. Nat. Sci.: Nanosci. Nanotechnol",2016.

[9] A.W.Bauer,W.M.M.Kirby,J.C.Sherris,M.Turck,"Antibiotic susceptibility testing by a standardized single disk method. Am J Clin Pathol",493–6,1996.

[10] V.S.Suvith, D.Philip,"Catalytic degradation of methylene blue using biosynthesized gold and silver nanoparticles", in Spectrochim Acta A Mol Biomol Spectrosc,526-532,2014.

[11] V.K.Vidhu and D.Philip, "Catalytic degradation of organic dyes using biosynthesized silver",2004.

[12] A.Ghadimi,R.Saidur and H.S.C.Metselaar, "A review of nanofluid stability properties and characterization in stationary conditions",in International Journal Heat and Mass Transfer,54:4051-4068 and nanoparticles Micron 56: 54-62,2011.

[13] D.H.Jain,D.Kumar,S.Kachhwaha,S.L.Kothari,"Synthesis of plant-mediated silver nanoparticles using papaya fruit extract and evaluation of their antimicrobial activities. Dig J Nanomat Bios,557-563,2009.

[14] T.Elavazhagan,K.D.Arunachalam, "Memecylon eduleleaf extract mediated green synthesis of silver and gold nanoparticles",in International Journal of Nanomedicine,1265–1278,2011.

[15] S.Link,M.A.EI-Sayed,"Optical properties and ultrafast dynamics of metallic nanocrystals", in Annual Rev Physical Chemistry,331-366,2003.

[16] D.N.DeAssis,V.C.Mosqueira,J.M.Vilela,M.S.Andrade,V. N.Cardoso, " Release profi les and morphological characterization by atomic force microscopy and photon correlation spectroscopy of 99m Technetium—fluconazole nanocapsules",in International Journal of Pharmacy,349:152–60,2008.

[17] H. Lachheb, E.Puzenat,A.Houas,M.Ksibi,E.Elaoui,G.Gullard,J.M.Hermann,"Photocatalyticdegradationofvarioustypesofdyes(alizarinS,creceinOrange G, methyl red, congo red, methylene blue) in water by UV-irradiated titania", Appl. Catal. B: Environ.,75–90,2003.

[18] T.Shahwan,S.A.Sirriah,M.Nairat,E.Boyacı,A.E.Eroğlu,T. B.Scott and K.R.Hallam,"Chem. Eng. J",2011.

[19] A.Rauf,M.A.Meetani,A.Khaleel and A.Ahmed ,"Chem. Eng. J",2010.

[20] M.Mahmoud,A.Poncheri,Y.Badr and M.Abd el Wahed, " South African Journal Sci.",105 299,2009.

[21] Z-C Wu, Y.Zhang, T-X Tao, L.Zhang and H.Fong , "Appl. Surf. Sci",2010.