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BIO-DERIVED SILVER NANOPARTICLES FOR CATALYTIC OXIDATION OF ALDEHYDE INTO ACID: AN ECOFRIENDLY APPROACH

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ABSTRACT:
Nanoparticles synthesis is new, speedy, eco-friendly, and safe trend in the field of nanotechnology. We demonstrated a simple and green chemical method has been carried out towards laboratory synthesized silver nanoparticles from Azadirachta Indica (Neem leaves) fruit and its application as a nano catalyst in oxidation of aldehyde to the corresponding carboxylic acid is reported here. The characterization of silver nanoparticles was confirmed using IR, SEM, TEM, U.V visible spectrometer. The synthesized Ag-NP are efficiently utilised in the oxidation of aldehyde to the corresponding carboxylic acid in presence of 40% NaOCl with high yield. The utilization of the Ag-NPs in the oxidation reaction is environment friendly condition is the novelty in this study.

Keywords: - Silver nanoparticles, Green Synthesis, Oxidation.

INTRODUCTION :

Silver nanoparticles are immensely used in various field including health care, food, consumer, and industrial purposes due to their unique chemical and physical properties. These include thermal, electrical, optical and high electrical conductivity and biological properties.[1-3] Due to their peculiar applications such as medical devices, optical sensor, cosmetics and pharmaceuticals, food industries, orthopaedic drug delivery as anticancer drug.[4] Recently silver nanoparticles used in many textile, biomedical divices, wound dressing.[2,5,6]Nanoparticles are unique and considerably change physical, biological and chemical properties due to their surface to volume ratio hence, these nanoparticles have been exploited for various purposes.[7,8]The oxidation of aldehyde was first reported by Rabiquet et al. and was attributed to water and air.[9]Although there are various methods for oxidation of aldehyde into acid, only few are amenable to broad range of functional group.[10]Due to high cost of complex oxidizing agent, hazardous nature of mettalic reagent or complex experimental condition are significant drawbacks.[11]There are various reagent are commercially available but expensive, in others the work up was difficult or the yield was unsatisfactory. Herein we report a method for preparation of carboxylic acid from aldehyde using inexpensive sodium hypochlorite in water gives molecular chlorine and oxygen both with oxidant properties.

EXPERIMENTAL :

MATERIAL AND METHODS :

The solvent like ethylacetate, acetone, acetonytrile, toulene, methanol, DMSO, DMF,Chloroform and Silver nitrate were purchase from Qualigen India. Mumbai. All chemicals and solvents used in the present work were of analytical reagent (A.R. grade) The double distilled water was used.

Apparatuse

The thin layer chromatography was executed on silica gel G. Boiling point of the aldehyde were confirmed by open capillary techanique. FTIR spectral analysis was performed and recorded

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using Shimadzu FTIR spectrometer using KBr Pellets. Proton and NMR spectra were recorded on a Brucker AVII FTIR spectrometer operating at 400MHz for the entire sample.

Preparation of Ag-Nps

Preparation of extract from Azardirachta indica choped Neem fruits:

Fresh Neem fruits were collected from college campus area. Fruits were thoroughly washes in running water to remove the dirt and dust on the surface of the fruits.20 gm of finely chopped Neem fruits were added to 50 mL of doubled distilled water and boiled for 10 mins. The extract was cooled and filterates and store for further use. This solution was used for green synthesis of silver nanoparticles (Ag-Np) is reducing the silver ions.

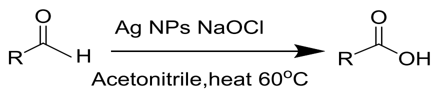
Preparation of Silver nanoparticles:

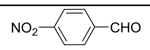
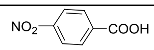
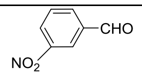
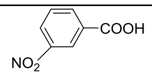
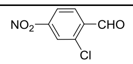
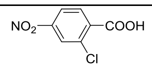
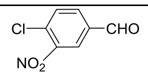
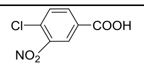
The aqueouse solution of double distilled $AgNO_3$ (1mM) was prepared and used for further synthesis of silver nanoparticles. 25mL of chopped fruit extract was slowly added in 100mL of 1mM $AgNO_3$ solution with constant stirring for reduction of Ag^+ ions. The mixture was stirred for 10min at 60ᵒc. The absorbance of the resulting solution was measured spectrophotometrically.

General Procedure for catalytic Oxidation of aldehyde into acid:

For model reaction,Benzaldehyde (0.02mM) and NaOCl (40% vol.of water) aetonitrile (25mL) and silver nanocatalyst (30µg/mL) were taken in 250mL Round bottom flask and stired at 60ᵒc. For 20 min. Oxidation of aldehyde into acid in presence of sodium hypochloride as an oxidising agent and acetonitrile as solvent. (Scheme I) The progress of reaction was analysed by TLC under U.V.TLC analyzer. The boiling point of synthesized product were determined by open capillary method. Catalyst was recovered by the filtering the mixture recrystalised and used for the next cycle. The spectral Charecterization of the acid were confirmed by IR, ^{1}HNMR,^{13} CNMR, mass and elemental analysis.

Scheme:



Sr. No	Aldehyde	Acid	Time	Yield
1.			1hour	95%
2			2 Hour	87%
3			2.50 Hour	85%
4			5:00 Hour	82%

Syntheis of 4-nitrobenzoic acid:

Pale yellow solid, yield:95% m.p.294ᵒ C [$C_7H_5NO_4$]IR KBr λmax/cm^{-1}) 3113,3050,1684,1275,2578 cm^{-1}, ^{1}H NMR (400 MHz, $CDCl_3$ / DMSO-d6), δ8.47(s,1H-CH),8.45(1H- CH)8.40(2H-CH),11.0 (1H-OH) ^{13}C NMR (400 MHz $CDCl_3$) 153.1,136.3,123.8,131.2,123.8,131.2,169.3 Mass Spectrum (GC-MS) 167.02[M] CHN calc. C, 50.31; H, 3.02; N, 8.38; O,38.29.CHN found, C, 50.30; H, 3.01; N, 8.35; O, 38.17.

Synthesis of 3-Nitrobenzoic acid:

Off-white solid, yield:87% m.p.140ᵒ c[$C_7H_5NO_4$]IR KBr λmax/cm^{-1})3117,3045,1280,2575 cm^{-1}, ^{1}H NMR (400 MHz, $CDCl_3$ / DMSO-d6), δ 8.60(s,1H-CH),8.76(1H- CH)8.60(1H-CH), 7.92(1H-CH) 11.0 (1H-OH).^{,13}C NMR (400 MHz $CDCl_3$) 147.8,131.1,129.1,123.9,133.7,129.5,163.6Mass Spectrum (GC-MS) 167.02[M^+] CHN calc. C, 50.31; H, 3.02; N, 8.38; O,38.29CHN found, C, 50.29; H, 3.00; N, 8.36; O, 38.27

2-chloro-4-nitrobenzoic acid:

White solid, yield:85% m.p.168.98ᵒ c[$C7H_4ClNO_4$]IR KBr λmax/cm^{-1}) 3120, 3046,1678,1273,2574, cm^{-1}, ^{1}H NMR (400 MHz, $CDCl_3$ / DMSO-d6), δ 8.38(s,1H-CH),8.35(1H-

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CH)8.24(1H-CH),11.0 (1H-OH).,[13]C NMR (400 MHz $CDCl_3$) 135.9,154.5,137.9,124.1,121.9,132.6,164.8.Mass Spectrum (GC-MS) 200.98[M^+] CHN calc. C, 41.71; H, 2.00; N, 6.95;O,31.75,Cl,17.59.CHN found, C, 41.70; H, 2.00; N, 6.94; O, 31.74,Cl,17.57

4-chloro-2nitrobenzoic acid:

Yield:82% m.p.168.98° c[$C_7H_4ClNO_4$]IR KBr λmax/cm^{-1})3115, 3049,1683,1278,2576,cm^{-1}, [1]H NMR (400 MHz, $CDCl_3$ / DMSO-d6), δ 8.41(s,1H-CH),8.56(1H- CH)8.09(1H-CH),11.0 (1H-OH).,[13]C NMR (400 MHz $CDCl_3$) 138.8,150.3,124.2,124.1,134.8,132.6,164.0Mass Spectrum (GC-MS) 200.98[M^+] CHN calc. C, 41.71; H, 2.00; N, 6.95;O,31.75,Cl,17.58.CHN found, C, 41.70; H, 2.00; N, 6.94; O, 31.74,Cl,17.58

RESULT AND DISCUSSION:

U.V-Visible spectra:

A study of UV-vis spectra carried out in the range of 200-800 nm to determine surface plasmon resonance of the synthesized Ag-nano particles. The colour of the reaction mixture of Ag-nano particle changes to dark orange from yellow colour indicates formation of Ag-nano particles. The synthesized Ag-nano particle have SPR value at 415 .

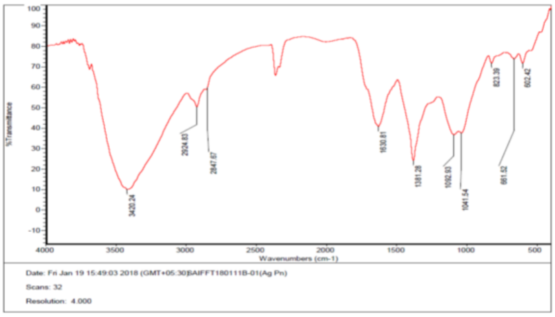
SEM Analysis of Silver nanoparticles:

The SEM image of Nanoparticles **Figure 3** showed cubical and relatively uniform shape of nanoparticles formation with diameter range **2 nm**. The larger silver particles may be due to the aggregation of the smaller ones, due to the SEM measurements.

TEM Analysis of Silver nanoparticles:

Figure 4 Shows the TEM image of AgNPs synthesized by using Azadirachta Indica (Fruit) extract which predominates with spherical triangle, truncated triangles, and decahedral morphologies ranging from 2 to 20 nm with an average size of **15.42 nm**. Most of the AgNPs were roughly circular in shape with smooth edges.

FT-IR Spectral analysis



The FT-IR shows different peaks at 3420,2924,2847,1630,1381,1041 cm^{-1} The FT -IR reveals different functional group hydroxyl -O-H stretching 3420 cm^{-1},aldehyde C-H streching2924cm^{-1} C-H bending 1381cm^{-1}. The peak near 823 cm^{-1} assigned to C- F and the peaks near 661 cm^{-1} and 602.42 cm^{-1} assigned to Ag nanoparticles[12]. A.Indica fruit extract possibly the hydroxyl group of these phytomolecule played a major role in the reduction of Ag ions to form Ag NPs. In the present investigation an eco-friendly, green, cost effective and simple approach in the syntheis of Ag-Np by using fruit of Azadirachta indica is demonstrated. The formation of Ag-Nps was confirmed by SEM, TEM, U.V. IR. Initial attempts to optimize the reaction condition for the oxidation of aldehyde into acid were done using benzaldehyde as substrate in presence of different solvents and sodium hypochlorite as oxidising agent and ((30µg/mL) Ag-Nps. We get best result in acetonitrile as solvent at 20min and get 93% yield. As compared to the other solvent as given in table 1.

Sr.No.	**Solvent**	**Time**	**Yield**
1	Acetonitrile	20 min	93%
2	Ethyl acetate	1hr	76%
3	Toulene	2hr	80%
4	DMSO	10hr	72%
5	DMF	8hr	75%
6	Chloroform	11hr	70%
7	Methanol	6hr	85%

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The catalytic application of synthesized Ag-Nps as a catalyst was recovered by simple filteration and washed with hot water/ethanol to remove and absorbed product. The activity of catalyst was observed five times, the catalyst was reused without loss of their catalytic acitvity.

CONCLUSION:

It is very simple, easy and ecofriendly process of synthesis of Ag-Nps using Azadirachta Indica(Fruit).We have developed an effective and inexpensive catalytic method for the oxidation of aldehyde into carboxyllic acid using Ag-Nps and NaOCl as oxidising agent with high yield product. The Ag-Nps were found to be highly active and recycled for consecutive runs without significant loss of catalytic activity.

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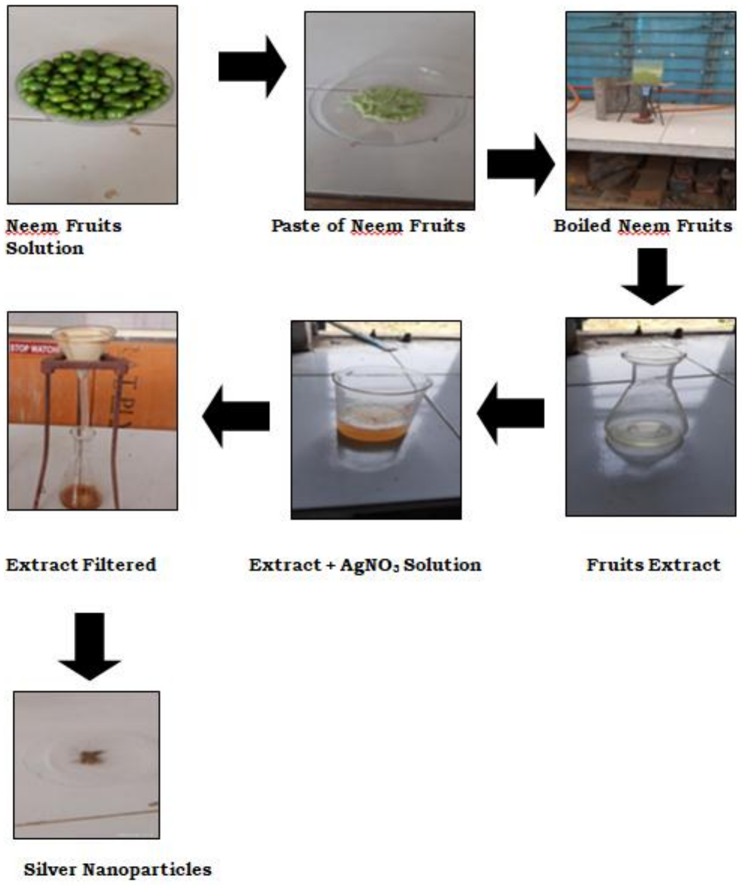

Fig.1: Preparation of the extract and synthesis of Silver Nanoparticle.

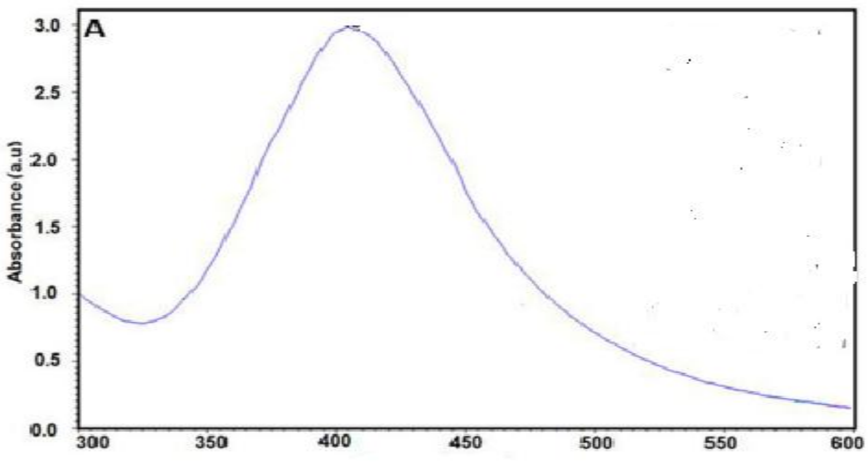

Figure 2: U.V spectra of silver nanoparticles

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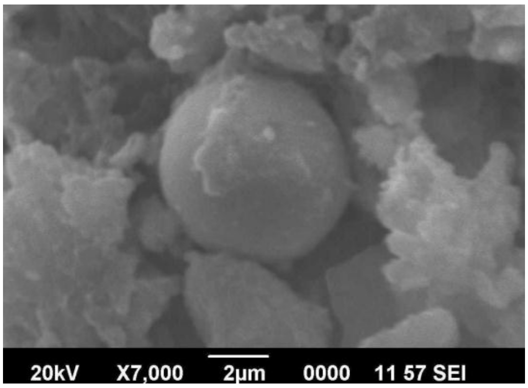

Figure 3: SEM image of Silver nanoparticles

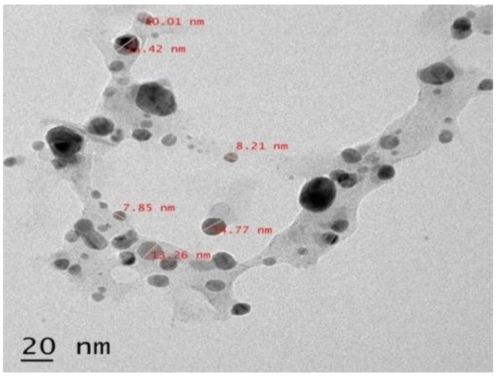

Figure 4: TEM analysis of synthesized silver nanoparticles

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