Title : Study of Synthesis , Characterisation and Photocatalytic degradation of Methyl orange using Copper Nanoparticles derived from roots of *Averrhoa carambola*.

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Abstract : Photocatalytic degradation using metal nanoparticles is one of the most preferred method to eradicate water contamination mainly caused due to toxic azo dyes. In this study, synthesis of Copper nanoparticles(CuNP's) is mainly discussed using aqueous extract of roots of *Averrhoa carambola*. Purpose of this study is to scientifically investigate photocatalytic efficacy of CuNP's. Synthesised CuNP's showed maximum wavelength at 278 nm after 30 minutes of synthesis. Fourier Tranform Infrared (FTIR) Spectroscopy results are obtained giving functional groups responsible in formation of CuNP's. Field Emission Gun - Scanning Electron Microscopy (FEG-SEM) showed particle sizes in the range of 32.8 nm, 33.8 nm, 38.5 nm and 47.8 nm for CuNP's .Whereas, Energy dispersive X-Ray spectroscopy (EDS) technique also determined presence and composition of synthesised CuNP's formed. Futher , its photocatalytic efficacy is highlighted against degradation of Methyl orange. To summarise, in this study green CuNP's proved to be an efficient nanocatalyst with 93.91 % degradation of methyl orange in six minutes.

Keywords : Copper nanoparticles, *Averrhoa carambola*, photocatalysis etc.

1.Introduction :

The area of science that studies materials at the nanoscale is called nanotechnology. Because of its uses in industries, agriculture, pharmacology, and other disciplines, it has become increasingly important with time[1-3].This branch has conducted extensive research including metal nanoparticles, carbon nanotubes, ceramics etc. Especially metal nanoparticles because of their special qualities have drawn a lot of attention for investigation. For example, Copper Nanoparticles is well known for its effective therapeutic and catalytic applications[4-6] . Metal nanoparticle synthesis can be achieved by a variety of techniques, including co-precipitation, sol-gel, ball milling, laser ablation, and green synthesis. Green metal nanoparticles can be synthesised using microbes or plant extracts[7-8] . In this study synthesis of copper nanoparticle has been discussed using roots of *Averrhoa carambola* also called as Star fruit. This plant is listed in tropical trees category and found in most of the parts of Asia. So far ,the metal nanoparticles synthesis using leaves and fruits of *Averrhoa carambola* have been reported but usage of its roots for the same have not yet explored[9-10]. This plant is itself known for its medicinal properties such as antibacterial, antifungal, antioxidant properties [11-12]. Further, green metal nanoparticles have contributed significantly as effective photocatalyst in dye degradation processes[13]. These dyes are group of azo dyes used mainly in textile industries. Methylene blue , Methyl orange , Alizarin red etc are some of the examples of azo dyes when released in water untreated which causes severe contamination

leading to harmful effects to environment and aquatic life as well[14]. These dyes are carcinogenic in nature and therefore degradation of such dyes during water treatment becomes important to reduce its toxicity[15].

2. Materials and Methods :

2.1 Collection of Plant Material :

Roots of *Averrhoa carambola (AC)* were collected from Bordi village located in Palghar district ,Maharashtra. These roots were thoroughly washed with normal water to remove mud and dirt . After initial washing , roots were soaked in crystal salt water for few minutes to remove any bacterial or fungal infestation. Then they were shadow dried for 20 days and stored in air tight glass containers until further use.

2.2 Synthesis of aqueous plant extract :

These dried roots were cut into pieces using scissors and then crushed in mortar and pestle manually. Approximately 2 gm of crushed roots were taken in 50 ml of distilled water and soaked overnight to follow maceration principle and allow percolation for better results. These soaked roots with its solution was concentrated by gently boiling at mild temperature till its volume is reduced to half of its quantity . This solution was filtered through Filter paper . The collected filtrate was used as Plant Extract.

2.3 Synthesis of Copper Nanoparticles:

1mM of Copper Sulphate ($CuSO_4.5H_2O$) was used as a precursor. $CuSO_4.5H_2O$ from Lobachemie company was used. 10 ml of prepared plant extract was added dropwise to 90 ml of $CuSO_4.5H_2O$ solution while stirring. $CuSO_4.5H_2O$ solution with plant extract solution was monitored in normal conditions where eventually it turned from colourless to brown which indicated the formation of CuNP's. Their maximum wavelength was measured using UV-visible spectrophotometer.

3. Characterisation Results:

3.1 UV – Visible Spectrophotometer - Maximum wavelength was measured using UV-Visible spectrophotometer of Shimadzu -1800 model. In this technique small aliquot of plant extract and synthesised CuNP's were measured after 30 minutes of its synthesis to find its maximum wavelength in the entire range of 800-200 nm spectrum mode. Refer Fig.3.1, Maximum wavelength of plant extract was found to be at 279 nm and CuNP's at 278 nm. Whereas, 1mM of $CuSO_4.5H_2O$ maximum wavelength was obtained at 365.50 nm .

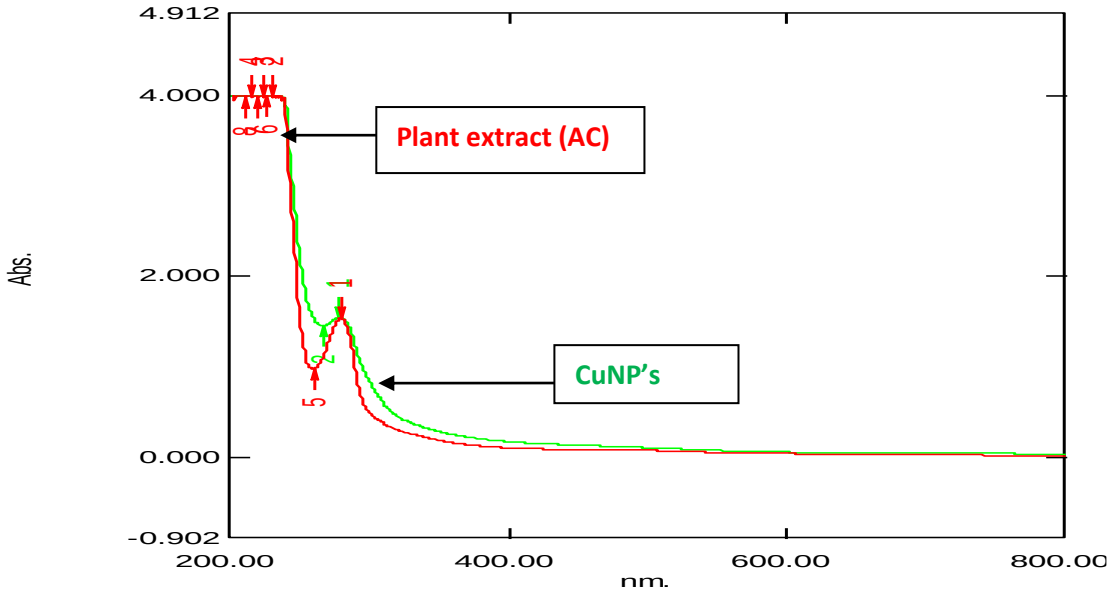


Fig.3.1 UV-Visible spectra of CA and CuNP's after 30 minutes of synthesis

3.2 FTIR analysis : In this technique ,functional groups were detected using Bruker Vertex 80 FTIR model. 100 µl of sample was loaded on Potassium Bromide (KBr) pellet and compressed in hydraulic pellet compressor. Pellets were then dried under Infra Red (IR) lamp for few minutes. These dried pellets were measured in the mid IR range of 400cm^{-1} to 4000cm^{-1} frequency.

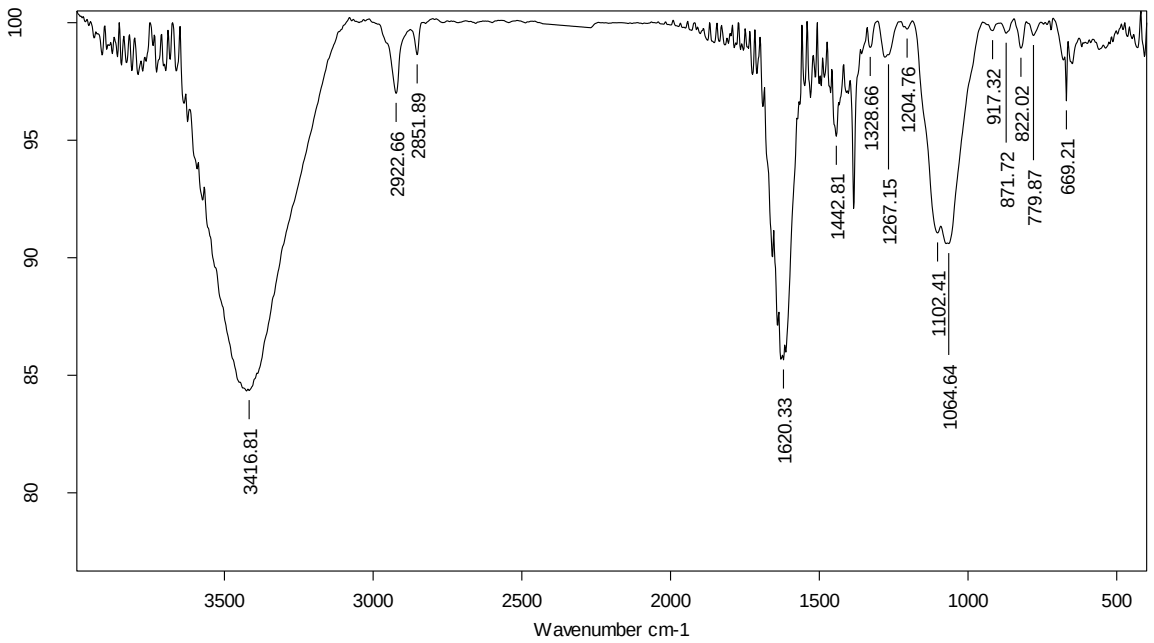


Fig. 3.2.a) FTIR spectra of CA.

Refer Fig. 3.2a) , In the Plant extract certain functional groups were seen such as 3416.81 cm^{-1} for Hydroxyl (OH) group, 2922.66 cm^{-1} and 2851.89 cm^{-1} for Aliphatic (C-H)

stretch,1620.33 cm^{-1} and 1442.81 cm^{-1} for alkenes (C=C stretch), 1328.66 cm^{-1} for NO_2 group , 1204.76 cm^{-1} , 1102.41 cm^{-1} ,1064.64 cm^{-1} for alkyl and aryl halides, 917.32 cm^{-1} for monosubstituted alkene ,871.72 cm^{-1} and 822.02 cm^{-1} for disubstituted phenyl ring , 779.87 cm^{-1} for trisubstituted alkene and 669.21 cm^{-1} for disubstituted alkene.

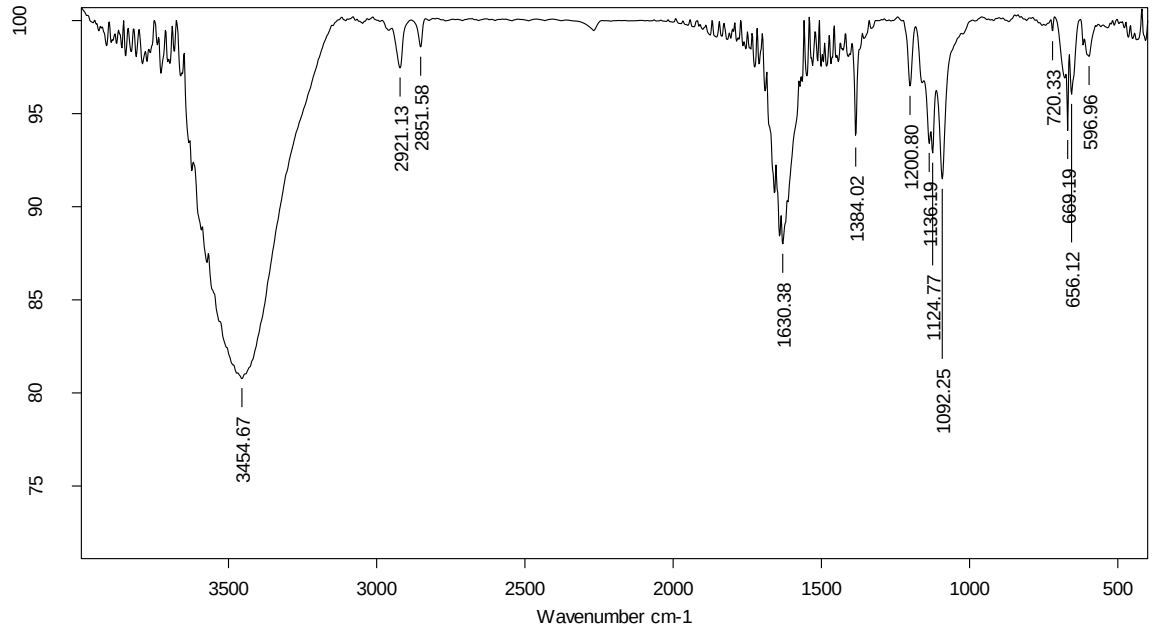


Fig. 3.2.b) FTIR spectra of synthesised CuNP's

From the above Fig.3.2b), obtained results it is found that functional groups present at 3442.67 cm^{-1} for Hydroxyl (OH) stretch ,2918.29 cm^{-1} and 2849.99 cm^{-1} for Aliphatic C-H stretch or alkanes, 1630.77 cm^{-1} for Alkene (C=C) and 1384.15 cm^{-1} for NO_2 group, 1201.00 cm^{-1} , 1136.50 cm^{-1} , 1124.80 cm^{-1} and 1092.46 cm^{-1} for Alkyl or aryl halides, 600.18 cm^{-1} for metal-ligand (M-L) stretch are responsible for the formation of CuNP's.

3.3.FEG-SEM : In this technique ,size determination was done using JEOL JSM-7600F FEG-SEM model after 24 hours of Synthesis. Synthesised CuNP's were loaded on carbon tape placed on stub. Loaded sample was dried in Infra Red (IR) lamps for 15 minutes. It was placed in Leica EM ACE600 model for platinum coating to enable charge effect for 20 minutes. Samples were placed in sample holder and images were scanned at different magnifications. Refer Fig.3.3,Sizes were determined using IMAGE-j software CuNP's of sizes 32.8 nm, 33.8 nm, 38.5 nm and 47.8 nm were obtained.

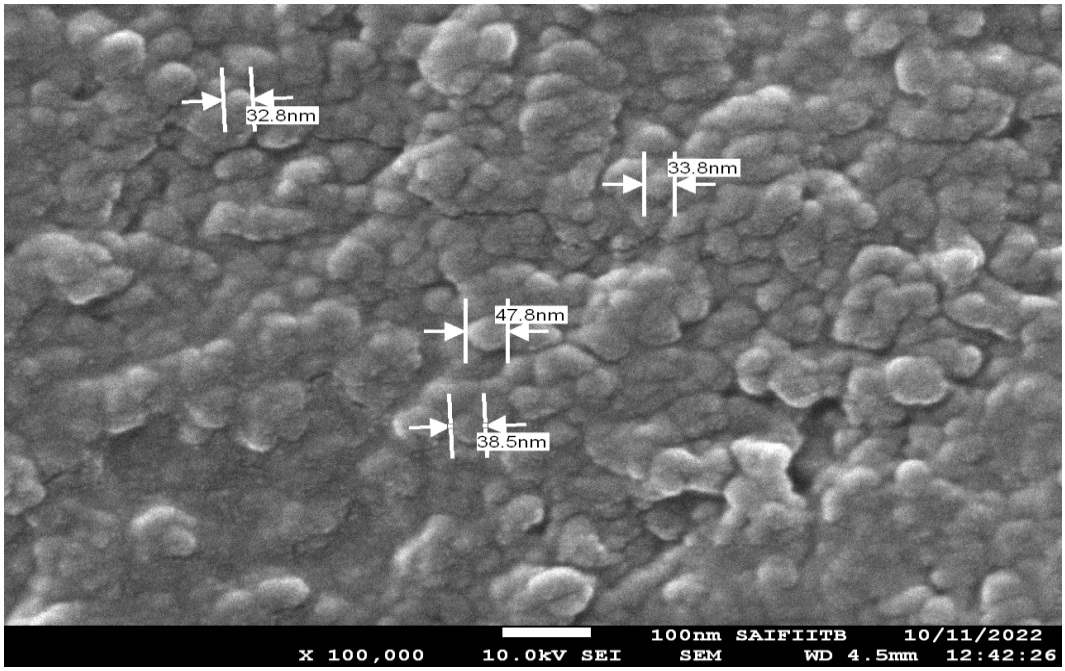
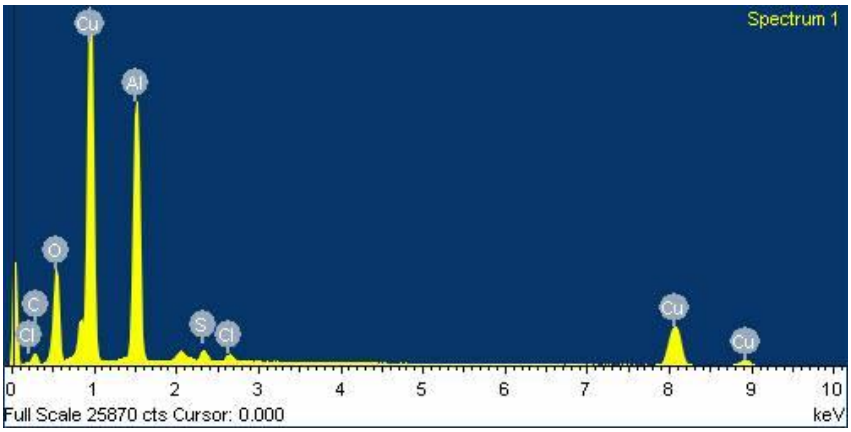


Fig. 3.3 FEG-SEM image of synthesised CuNP's

3.4 Energy dispersive X-Ray spectroscopy (EDS) : In this technique Samples were loaded on aluminium strip and dried in IR lamp for few minutes. It was coated with platinum to enable charge effect in Leica EM ACE600 model for 10 minutes. Samples were placed in sample holder and scanned for better image location and elemental composition detection was done using FEG-SEM instrument of JEOL JSM-7600F model. Below information in Fig.3.4 and Table 1 obtained alongwith the EDS spectrum confirms the presence of CuNP's in the sample.



Element	Weight%	Atomic%
C K	6.56	16.63
O K	15.81	30.09
Al K	23.39	26.40
S K	1.15	1.09
Cl K	0.89	0.77
Cu L	52.20	25.02
Totals	100.00	

Fig.3.4 EDS of CuNP's

Table 1

4.1 Dye degradation activity of CuNP's:

200 µl of CuNP's was added in 10 ml of 50 ppm of Methyl Orange (MO) in the presence of 200 µl of Sodium Borohydride ($NaBH_4$) solution. At first, initial absorbance reading(A_0) was recorded using UV-Visible Spectrophotometer and the reaction mixture was allowed to

react under visible light at room temperature and final absorbance reading(A_t) was recorded until the orange color and main peak of the Methyl orange dye diminishes.

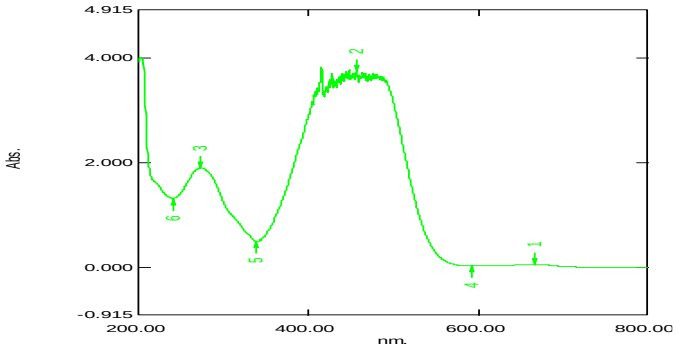


Fig.4.1a) UV-Visible Spectra of Methyl Orange at 455 nm

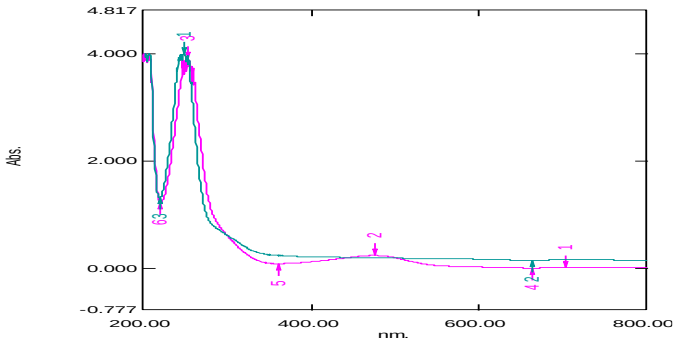


Fig 4.1b) UV-Visible Spectra of Photocatalytic Degradation of Methyl Orange using CuNP's.

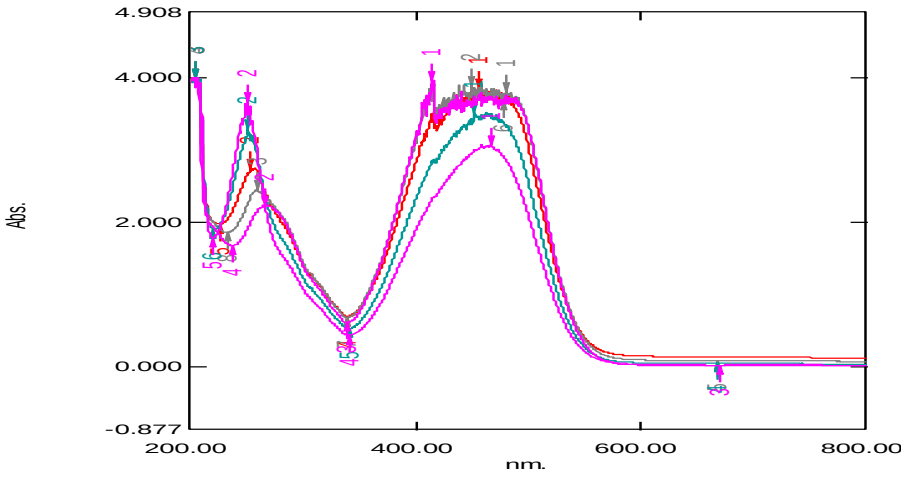


Fig 4.1c) UV-Visible Spectra of Degradation of Methyl Orange using CuNP's in dark

5.Discussions :

During EDS analysis after few months particle size aggregations were observed in scanned images. For dye degradation activity ,to overcome aggregation of CuNP's were sonicated once using using Ultrasonicator with tungsten probe[16]. However, to accelerate the dye

degradation process , $NaBH_4$ was added to activate the metal catalyst [17]. With the obtained initial and final absorbance values dye degradation in percentage was calculated using formula(1) Where , A_0 and At are the initial and final absorbance values.

$$\text{Degradation} = \frac{A_0 - At}{A_0} * 100 \qquad (1)$$

$$\text{Methyl Orange degradation} = \frac{A_0 - A_t}{A_0} \times 100 = 93.91\ \%$$

From Fig.4.1a) Maximum wavelength of prepared 50 ppm Methyl orange solution was found to be at 455 nm which is close to recorded value of λ max at 464 nm of Methyl Orange. In Fig.4.1b) , It was found that CuNP's could degrade 93.91 % of methyl orange in 6 minutes. Refer Fig.4.1c) Whereas, reaction mixture placed in dark conditions could degrade 22.58% of the dye in 15 minutes. IUPAC name of Methyl orange is dimethylaminoazobenzenesulfonate and is an anionic dye which contains aromatic and –N = N– groups in their molecules. It is known for its high toxicity, carcinogenic and teratogenic effects, and is harmful to the environment and organisms[18]. From overall discussions, it is scientifically proven that CuNP's played effective catalyst role in the presence of light to degrade Methyl Orange.

6. Conclusion and future perspective :

From the above results and discussions, it can be concluded that green CuNP's could degrade methyl orange peak effectively only in six minutes. From this study, it has proved that CuNP's acts as an efficient photocatalyst with associated advantages like time saving, cost effective and also being environmental benign. Use of CuNP's is also considered to be more economical compared to other rare and noble nanoparticles due to its abundant presence in nature. Currently I am reporting monometallic nanoparticles photocatalytic dye degradation studies, I have also completed bimetallic nanoparticles approach towards photocatalytic dye mixtures degradation studies which will be reflected in my PhD thesis. In future, I prefer to use green waste as bioreductants in corresponding metal precursors to study sustainable approaches to conserve ecosystem and design remedial measures towards environmental concerns.

7. Acknowlegments

I would like to acknowledge SAIF-IITB, Powai, Mumbai for allowing me to visit their laboratory analysis during my sample analysis.

8. Conflicts of Interest

I declare no conflicts of Interest.

List of abbreviations used :

1. Copper nanoparticles : CuNP's

2. UV : Ultra -Violet
3. Fourier Tranform Infrared : FTIR
4.Field Emission Gun -Scanning Electron Microscopy : FEG-SEM
5.Energy dispersive X-Ray spectroscopy : EDS
6. *Averrhoa carambola* – AC
7. Methyl Orange - MO

References :

[1]i. Vasconcelos and t. Santos, "nanotechnology applications in sepsis: essential knowledge for clinicians," pharmaceutics, vol. 15, no. 6, p. 1682, jun. 2023, doi: 10.3390/pharmaceutics15061682

[2] Srinivas, Pothur r et al. "nanotechnology research: applications in nutritional sciences." *The journal of nutrition* vol. 140,1 (2010): 119-24. Doi:10.3945/jn.109.115048
[3] Malik, Shiza et al. "nanotechnology: a revolution in modern industry." *Molecules (basel, switzerland)* vol. 28,2 661. 9 jan. 2023, doi:10.3390/molecules28020661

[4] S. A. Akintelu, et al. "green chemistry approach towards the synthesis of copper nanoparticles and its potential applications as therapeutic agents and environmental control." Current research in green and sustainable chemistry,volume 4,2021,100176,issn 2666-0865,https://doi.org/10.1016/j.crgsc.2021.100176

[5] Ahmed, Inas a et al. "investigation the effects of green-synthesized copper nanoparticles on the performance of activated carbon-chitosan-alginate for the removal of cr(vi) from aqueous solution." *Molecules (basel, switzerland)* vol. 26,9 2617. 29 apr. 2021, doi:10.3390/molecules26092617

[6] Nzilu, D.M., Madivoli, E.S., Makhanu, D.S. *et al.* Green synthesis of copper oxide nanoparticles and its efficiency in degradation of rifampicin antibiotic. *Sci rep* **13**, 14030 (2023). Https://doi.org/10.1038/s41598-023-41119-z

[7] Shahid-ul-islam et al.,"review on green biomass-synthesized metallic nanoparticles and composites and their photocatalytic water purification applications: progress and perspectives"chemical engineering journal advances,volume 14,2023,100460,issn 2666-8211,https://doi.org/10.1016/j.ceja.2023.100460

[8] M. Khatun et al."green synthesis of silver nanoparticles using extracts of mikania cordata leaves and evaluation of their antioxidant, antimicrobial and cytotoxic properties"food chemistry advances,volume 3,2023,100386,issn 2772-753x, https://doi.org/10.1016/j.focha.2023.100386

[9] A. Bangaru Babu, k. durga bhavani anagani & P. sravanthi. (2023) green synthesis of gold nanoparticles using carambola fruit extract and evaluation of their antioxidant and anticancer efficiency. *Asian journal of chemistry* 35:3, pages 739-747.

[10] S. Chakraborty et al."Averrhoe carrambola fruit extract assisted green synthesis of zno nanoparticles for the photodegradation of congo red dye"surfaces and interfaces,volume 19, 2020,100488,issn 2468-0230,https://doi.org/10.1016/j.surfin.2020.100488

[11] Lakmal k, Yasawardene p, Jayarajah u, Seneviratne sl. "Nutritional and medicinal properties of star fruit (*averrhoa carambola*): a review." Food sci nutr. 2021 jan 23;9(3):1810-1823. Doi: 10.1002/fsn3.2135. Pmid: 33747490; pmcid: pmc7958541

[12] muthu, narmataa et al. "nutritional, medicinal and toxicological attributes of star-fruits (averrhoa carambola l.): a review." *Bioinformation* vol. 12,12 420-424. 22 dec. 2016, doi:10.6026/97320630012420

[13] k. P. Gopala et al."Photocatalytic activity induced by metal nanoparticles synthesized by sustainable approaches: a comprehensive review" ,frontiers in chemistry,10(2022) 2296-2646 ,doi=10.3389/fchem.2022.91783

[14] dacic, armina & hindija, lamija & karačić, alma. (2020). Toxicity of azo dyes in pharmaceutical industry. 10.1007/978-3-030-17971-7_88

[15] kumari, harita et al. "a review on photocatalysis used for wastewater treatment: dye degradation." *Water, air, and soil pollution* vol. 234,6 (2023): 349. Doi:10.1007/s11270-023-06359-9

[16] C. Chiew et al. "functional liquid metal nanoparticles: synthesis and applications",material advances, 2021, **2**, 7799-7819, doi: 10.1039/d1ma00789k

[17]b. Y. Buyukakinci and n. Sokmen, "investigation of indigo dyeing using sodium borohydride as reducing agent," cbup, vol. 5, pp. 1061–1063, sep. 2017, doi: 10.12955/cbup.v5.1071

[18] Wu, L., Liu, X., Lv, G. *et al.* Study on the adsorption properties of methyl orange by natural one-dimensional nano-mineral materials with different structures. *Sci Rep* **11**, 10640 (2021). https://doi.org/10.1038/s41598-021-90235-1