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Study the Characterization and Preparation of Silver Nanoparticle using Friendly Green Synthesis

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Abstract

The synthesis of silver nanoparticles (AgNPs) has been made more economically feasible and environmentally friendly by use renewable and non-toxic Litchi chinensis as a capping and reducing agent instead of chemical reducing agents. to convert silver ions into silver nanoparticles. X-ray diffraction (XRD) and UV-Vis spectrophotometry (UV-Vis spectrophotometry) were used to study the resulting silver nanoparticles. The face-center-cubic (FFC) structure of the produced silver particles is evident from the X-ray diffraction study.

Keywords: Litchi Chinensis Extract, Silver Nanoparticles, FFC and XRD.

1. Introduction:

As their characteristics might differ greatly from those of their respective bulk metals, metal nanoparticles such as copper, gold, platinum, and silver have received a lot of attention lately. The optical and electrical properties of these metal nanoparticles are dependent on their size. Due to its distinct size- and shape-dependent optical, electrical, and catalytic capabilities, silver (AgNPs) is the most well-known of several nanomaterials that have gained attention recently [1]. The environmentally benign, cost-effective, and environmentally friendly process of employing plant extract for the green production of silver nanoparticles (AgNPs) is gaining popularity [2]. Researchers have become interested in nanoparticles of sizes between 1 and 100 nm for their optical, chemical, and mechanical characteristics[3]. Numerous applications, including those in the agricultural, pharmaceutical, industrial, and medical sectors, have been proposed [4].

Several chemical and physical processes, including as chemical reduction, thermal breakdown, electrochemistry, son chemistry, microwave energy, laser ablation, helium droplets, and sol-gel, can produce metal nanoparticles[5-7]. These methods could affect the environment badly because they used hazardous chemicals and solvents. However, in recent years, a new technique has been utilized to produce different metal and semiconductor nano-objects, which is called green synthesis[8, 9]. This method depends on using different plant portions and bio-organisms such as fungus, yeast and bacteria to form nanoparticles[10]. It is expected that the bioactive compound which exist in plants and microbes could serve as capping and reducing agents.

Plant extract technique has more advantages when compared to other biological procedures, because it doesn't require culturing processes[11]. Furthermore, nanoparticles formed using plant extract methods are favored since they are

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profitable, single-step process for biosynthesis process and environment friendly[12]. Al Hindawi groups created silver particles by extracting the peel from grapefruits (citrus paradise)[8]. Additionally, silver nanoparticles with an FFC phase structure and a diameter of 65 nm were effectively created utilizing bitter orange peel extract[13]. Dyes are a group of organic chemicals that are frequently employed in the culinary, printing, and textile industries. The majority of dye effluents are poisonous and non-biodegradable, and they all have a significant detrimental impact on the environment. Reactive red dye is a carcinogenic and poisonous derivative of phenothiazine that is used to color fabrics[14].

In this paper, using *Litchi chinensis* extract, which is an active fruit with various bioactive components like phenols and flavonoids. To characterize the resulting silver particles, an X-ray diffraction technique (XRD) and UV-visible spectrometer were used. Photo-degradation ability of our prepared Ag nanoparticles was studied. The results show that biosynthesized Ag nanoparticles can act as a photocatalytic to remove toxic congo red dye from wastewater.

2. Materials and Methods:

2.1 Synthesis Of Silver Nanoparticles:

At this project, deionized water was used as a solvent for dissolving starting materials. A solution of AgNO_3 (2mM) was prepared by adding silver nitrate into 200 mL distilled water and stirred for 30 minutes until no particle was observed. This solution was kept in a dark place to avoid the oxidation of silver. To prepare *Litchi chinensis* extract solution:

- 1- *Litchi chinensis* was washed with distilled water and cut into small pieces.
- 2- Allowing these small *Litchi chinensis* pieces to dry in oven at 75 °C.
- 3- Ten grams of the powdered *Litchi chinensis* were dissolved in 100 milliliters of distilled water, the proper amount.
- 4- The mixture was then heated to 80 °C for ten minutes, filtered and finally stored at ~6 °C.

(10 ml) of the *Litchi chinensis* extract solution and (90 ml) of the silver nitrate solution were combined

to create silver nanoparticles. Subsequently, this solution was stirred and kept for 6 hours at room temperature. The spectra of the solution were then captured using the UV-Vis spectrometer. The solution was centrifuged at 3000 r

pm for 45 minutes to prepare for SEM and XRD experiments, after which the sample was dried at 75 °C. Figure (1):

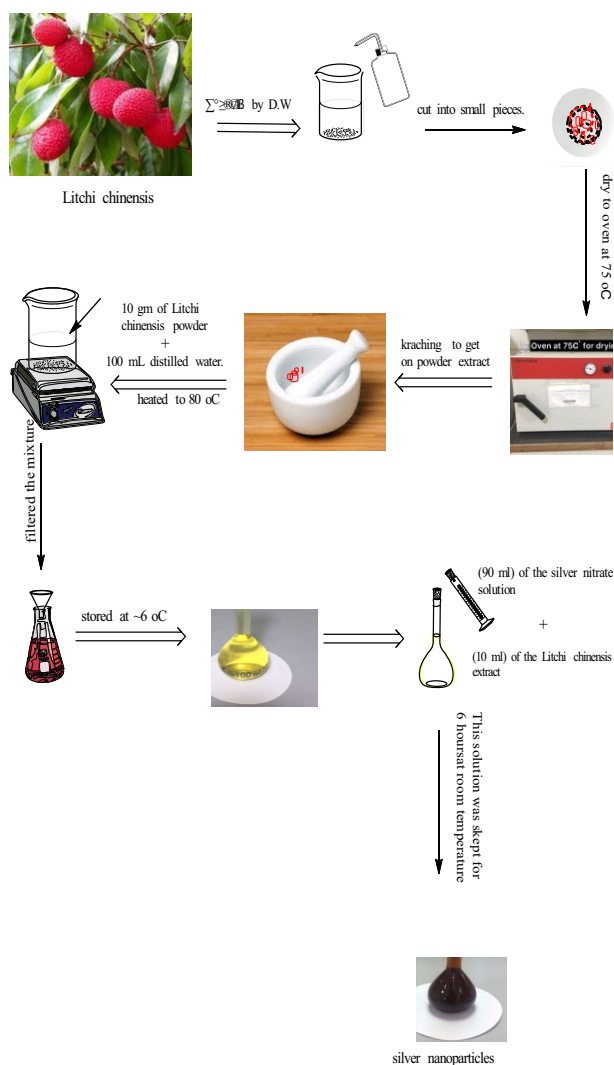


Figure 1: Suggested scheme of synthesis Ag Nps.

2.2 Photodecoloration of Congo Red Dye:

As the sodium salt of 3,3'-([1,1'-biphenyl]-4,4'-diyl) bis (4-aminonaphthalene-1-sulfonic acid), Congo red is an organic substance. The dye is an azo. Because Congo red dissolves in water, a red colloidal solution is produced; It is more soluble in organic solvents. Using this approach, 100 ml of congo red dye solution—the proper concentration of 100 ppm—was mixed with 0.1 g of AgNO₃ to make congo red solution (CR), figure (2) [15]. The produced suspension solutions were subjected to $1.41 \times 10^{-6} \text{ s}^{-1}$ Einstein UV-A light flux. To filter, around 3 mL of the suspension solution were obtained at different stages and centrifuged for 10 minutes at 4000 rpm. An absorption was then measured using the supernatant. The dye's UV Vis

spectrum measured at (496 nm).

A handmade photo reactor was used in an experimental setting to perform photocatalytic degradation. Irradiation sources (Philips mercury lamp UV(A), which has six 15-watt lights per lamp) (Germany). The majority of experiments were conducted in a 400 cm³ reactor. The distance between the lamp and the radiation vessel was fixed for a particular light intensity. The lamp was positioned perpendicularly above, figure (3). All studies involved using a magnetic stirrer to suspend the necessary amount of catalyst in 200 cm³ of aqueous dye solutions. In the majority of cases, and centrifuged (6000 rpm, 10 minutes) in a JANETZI - T5, Belgium centrifuge).

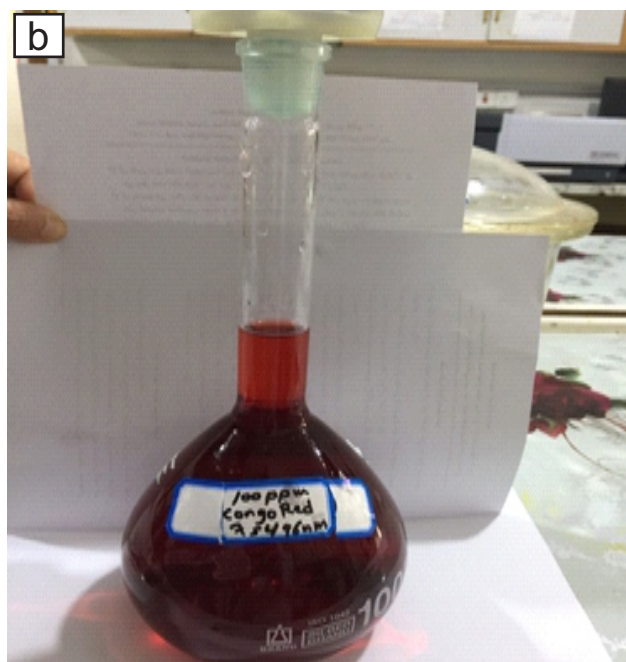
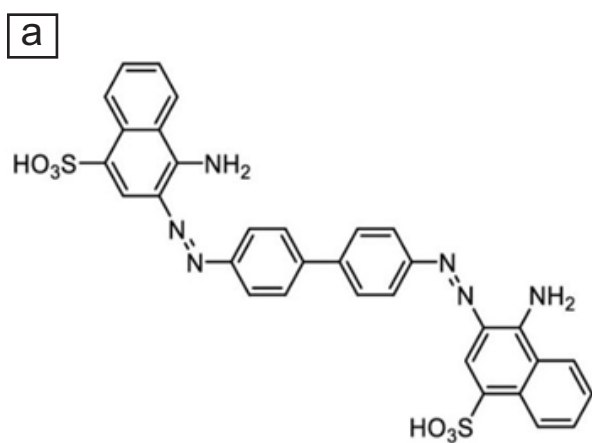


Figure 2: (a) Structure of Congo Red dye (b) A real image of preparation solution of Congo red in ppm.

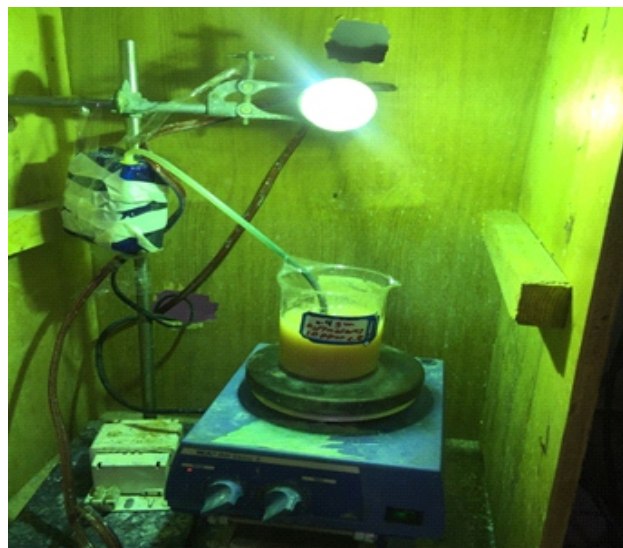


Figure. (3): Real image for (a) the reactor system without using UV-lamp, and (b) photo-degradation surface.

3. Results and Discussions:

Silver nitrate is made into a yellow solution when mango extract is added. Leaving the solution for (6 hours) under room temperature leads to change the color to brownish as shown in figure (1), indicating the formation of Ag NPs. silver nanoparticles. This changing means that silver ion is reduced by *Litchi chinensis* extract and free Ag was formed which growth to form cluster then nanoparticles.

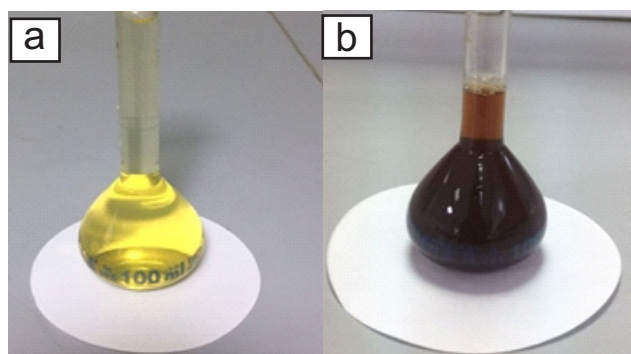


Figure (4): Prepared Ag nanoparticles from AgNO₃ and *Litchi chinensis* extract: (a) the solution after 0 hour mixing and (b) the solution after 6-hour mixing.

The UV-Vis absorption spectra provided confirmation that silver particles had formed (UV-Vis-1650PC Shimadzu, Japan). Figure (5) shows that the maximum absorption peak of Ag particles is centered around 400 nm, that means there is a blue shift about 20 nm when compared to bulk

silver[16]. The quantum size effect is responsible for this blue shift [17].

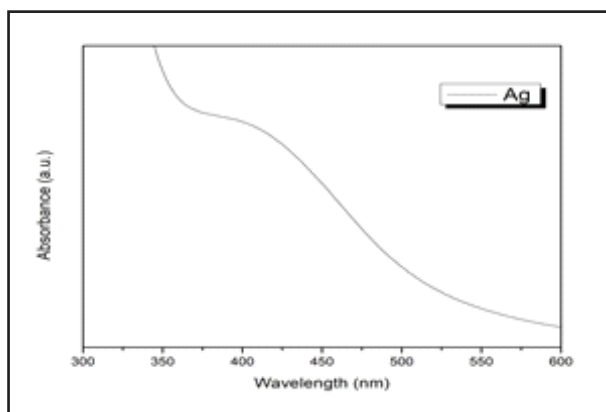


Figure. (5): The absorption spectra of Ag nanoparticles' when exposed to *Litchi chinensis* extract.

The crystalline makeup of the biosynthesized silver nanoparticles was examined using XRD analysis. The four peaks are pointed. See figure (6) were seen at $2\theta = 37.57^\circ, 42.71^\circ, 66.11^\circ,$ and 79.3° in the XRD pattern. The (110), (201), (223), and (314) planes, respectively, correspond to these diffraction peaks for Ag nanoparticles[18] suggesting the FCC phase structure for Ag nanoparticles. Using Scherrer's equation, the size of the silver nanoparticles is determined from the XRD data [19]:

$$D = \frac{K\lambda}{\beta \cos \theta} \dots \dots \dots (1) \P$$

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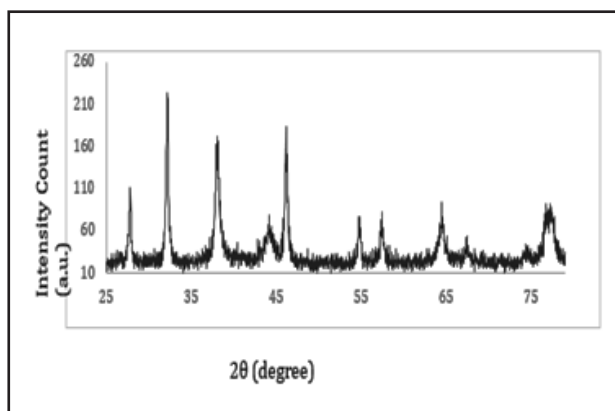


Figure 6: XRD pattern for Ag nanoparticles prepared using *Litch*

3.2 Photocatalytic Degredation Of Dye:

Studying Ag nanoparticles' photocatalytic activity. By irradiating the dye solution with UV light while also including AgNPs as a photo catalyst, it was possible to decolorize reactive red dye in solution. According to the following equations, the rate constant (k) of photocatalytic decolonization of Congo Red dye was calculated using the Langmuir-Hinshelwood expression for first order kinetics [19,20]

$$C_t = C_o \exp(-k_{app} \cdot t) \quad (2)$$

$$\ln\left(\frac{C_o}{C_t}\right) = k_{app} \cdot t \quad (3)$$

Here, Figure (7) shows the dye's beginning concentration (in mg/L) as C_o and its final concentration (in mg/L) during the time period of radiation exposure.

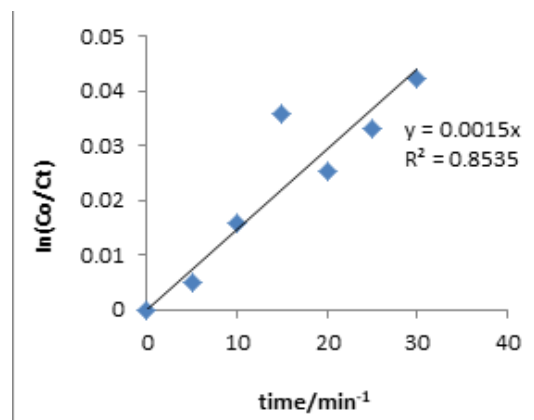


Figure 7: Relationship between the irradiation time and $\ln C_o/C_t$.

The photocatalytic decolonization efficiency (PDE) of the dye in the presence of AgNPs is calculated using the following equation:[21]

$$PDE = \frac{(C_o - C_t)}{C_o} \times 100\% \quad \text{----- (4)}$$

Figure. (8) shows that the PDE curve gradually increases with time, with the best PDE being achieved after irradiation for 10 And 30 min.

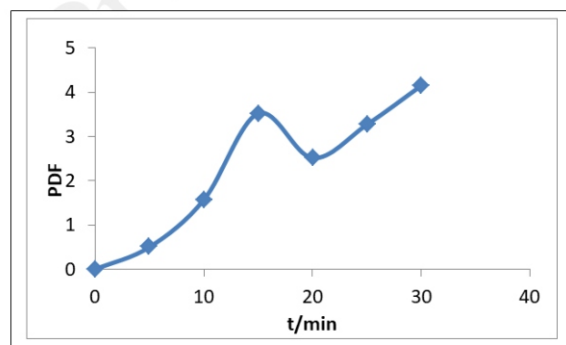


Figure. (8): Showing the PDE as a function of time.

3.3 Effect of Congo Red Dye Concentration:

To investigate the impact of the initial concentration of dye, various CR from (10-15) ppm concentrations were chosen. In figure (9), The rate of CR degradation is significantly influenced by the principal constituent of the dye solution. The photocatalytic degradation of dye with respect to time and concentration. As illustrated in Figure 4, the experimental results could be evaluated assuming pseudo first order kinetics,

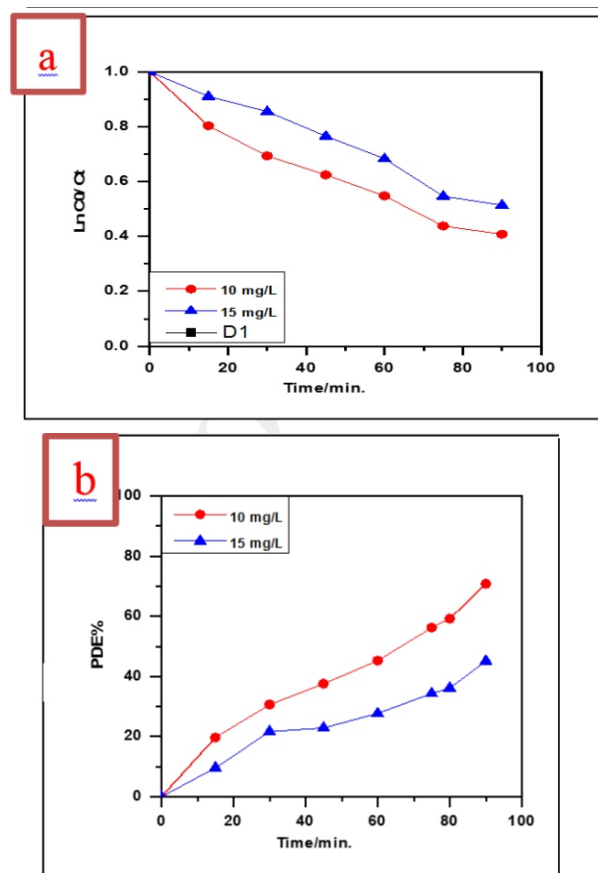


Figure 9: (a) The change in photocatalytic degradation and (b) PDE% as a function of concentrations caused by the starting concentration of CR dye.

Encouraging all quantity barriers to complete molecular transport between the aqueous and solid phases is largely dependent on the primary concentration [22]. This study deviates from Mahalakshmi, S., et al. (2015), who demonstrated a similar trend with an increase in the tenth day and a drop in the fifteenth day. All of the dye concentrations displayed a sharp decline in the amount of chlorophyll-a. [23].

3.4 Effect Solvent on the Congo Red Dye:

Within 105 minutes, the photocatalytic degradation of the Congo Red dye at various H_2O_2 and methanol concentrations was investigated in the presence of 0.4 gm, 10 ppm CR dye, 15.4 mW.cm⁻², and 298 K temperature. The kinetics of the reaction resembled those that were seen

in the absence of the oxidant. According to the experimental data, the reaction kinetics, as depicted in figure, follow first order kinetics (10).

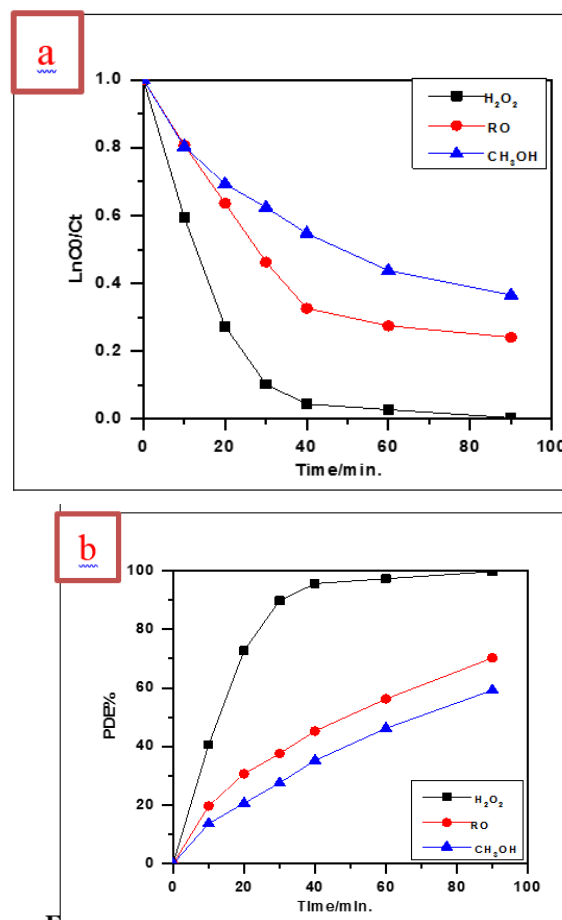
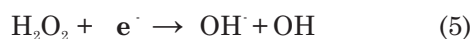


Figure 10: (a) PDE% as a function of scavenger type and (b) the solvent effect (H_2O_2 and CH_3OH).

The quantity of H_2O_2 at which hydroxyl radicals are produced has a limit. OH do not participate in oxidative pathways; instead, they are consumed in other reactions. As a hole scavenger, CH_3OH reacts with holes produced by photosynthesis to slow down the pace of deterioration. radicals in OH [24]. Hydrogen peroxide has two roles. It has two functions: first, it can generate; second, it can act as an electron acceptor, so promoting charge separation. OH radicals in accordance with the subsequent formulas [25].



Methanol finds extensive application in the industrial sector as a solvent and as a starting point for the production of formaldehyde, fuels, anti-freezing solvents, inks, dyes, resins, and adhesives [26].

4. Conclusions:

Silver nanoparticles was synthesized successfully from cheap, simple and eco-friendly method. Silver nanoparticles are prevented from aggregating by the *Litchi chinensis* extract's decreasing and capping effects. The bio synthesized particles have crystalline structure (FCC phase) and have the ability to degradation the Congo red dye.

References:

1. I.M. Krishna , G.B. Reddy, G. Veerabhadram, and A. Madhusudhan. "Eco-friendly green synthesis of silver nanoparticles using *Salmalia malabarica*: synthesis, characterization, antimicrobial, and catalytic activity studies." *Applied Nanoscience* 6 (2016): 681-689.
2. A.O. Dada, I. Adejumoke, E.I. Idu, O.M. Bello, A.P. Oluyori, A. Tabitha, A. Akande, A.A. Okunola, and O. Dada. "Effect of operational parameters, characterization and antibacterial studies of green synthesis of silver nanoparticles using *Tithonia diversifolia*." *PeerJ* 6 (2018): e5865.
3. J. Sivakumar, C. Premkumar, P. Santhanam, and N. Saraswathi. "Biosynthesis of silver nanoparticles using *Calotropis gigantea* leaf." *Afr. J. Basic Appl. Sci* 3, no. 6 (2011): 265-270.
4. D. Preetha, P. Kumari, C. Aarti and A. Renganathan. "Synthesis and characterization of silver nanoparticles using cannonball leaves and their cytotoxic activity against MCF-7 cell line." *Journal of nanotechnology* 2013 (2013).
5. F. Cheng et al., "Formation of Au and tetrapyrrolyl porphyrin complexes in superfluid helium." *Physical Chemistry Chemical Physics* 17, no. 26 (2015): 16699-16704.
6. N. Shiltagh et al., "Studying the optical properties of silver nitrates using a pulsed laser deposition technique." In AIP Conference Proceedings, vol. 2290, no. 1. AIP Publishing, 2020.
7. A. Hamzah, A. Hiba, A.M. Hindawi, and F.F. Al-Qaim. "SnO₂ nanoparticles: Synthesis, characterization and their applications in removing drugs from aqueous solutions." *Journal of Nanostructures* (2023).
8. A.Q. Abed, A.M. Alhindawi, and H. F. Alesary. "Green synthesis of zinc sulfide nanoparticles for the removal of methylene blue dye from aqueous solution." *Nano World J* 8 (2022):
9. Z.T. Turki, A.M. Alhindawi, and N. M. Shiltagh. "Green Synthesis of CdS Nanoparticles Using Avocado Peel Extract." *NanoWorld J* 8, no. 3 (2022): 73-78.
10. A.M. Alhindawi, I. Joudah, S. Hamzah, and Z. Tarek. "Plant extract: safe way for fabrication silver nanoparticles." In IOP Conference Series: Materials Science and Engineering, vol. 571, no. 1, p. 012069. IOP Publishing, 2019.
11. J.S. Tan et al., "A review on microalgae cultivation and harvesting, and their biomass extraction processing using ionic liquids." *Bioengineered* 11, no. 1 (2020): 116-129.
12. M.A. Irshad, R. Nawaz, M.Z. Rehman, , Synthesis, characterization and advanced sustainable applications of titanium dioxide nanoparticles: A review. *Ecotoxicology and environmental safety*. 212: p. 111978. 2021
13. M.A. Alhindawi, N. H. OBAID, I. JOUDAH, N. SHILTAGH, and K.J. TAHIR. "Fabrication and Characterization of Silver Nanoparticles Using Plant Extract." *International Journal of Pharmaceutical Research* (09752366) 12, no. 2 (2020).
14. S. Ouni et al., "A Novel Green Synthesis of Zinc Sulfide Nano-Adsorbents Using *Artemisia Herba Alba* Plant Extract for Adsorption and Photocatalysis of Methylene Blue Dye." *Chemistry Africa* (2023): 1-13.
15. A. Attia, A. Meguid, M.A. Hamid, A.A. Khedr, and N.A. Hassan. "Fixed-bed column studies for the removal of Congo red using *Simmondsia chinensis* (Jojoba) and coated with Chitosan." *Indonesian Journal of Chemistry* 18,

- no. 2 (2018): 294-305.
16. P. Pallela et al., "Ultra Small, mono dispersed green synthesized silver nanoparticles using aqueous extract of *Sida cordifolia* plant and investigation of antibacterial activity." *Microbial Pathogenesis* 124 (2018): 63-69.
 17. M.A. Marzouk, and S. M. Abo-Naf. "Structure characterization and photoluminescence of sol-gel synthesized Ag-Dy-codoped silica phosphor." *Journal of Non-Crystalline Solids* 505 (2019): 292-300.
 18. S.V. Otari, R.M. Patil, N.H. Nadaf, S. J. Ghosh, and S.H. Pawar. "Green biosynthesis of silver nanoparticles from an actinobacteria *Rhodococcus* sp." *Materials Letters* 72 (2012): 92-94.
 19. J. Jenkins, and L. Robert "Introduction to X-ray Powder Diffractometry (Volume 138). NY, John Wiley & Sons, 1996.
 20. F.F. Karam, H.M. Saeed, A.A. Yasasri, L. Ahmed, and H. Saleh. "Kinetic study for reduced the toxicity of textile dyes (reactive yellow 14 dye and reactive green dye) using UV-A Light/ZnO system." *Egyptian Journal of Chemistry* 63, no. 8 (2020): 2987-2998.
 21. S. Nethaji, A. Sivasamy and A.B. Mandal. "Adsorption isotherms, kinetics and mechanism for the adsorption of cationic and anionic dyes onto carbonaceous particles prepared from *Juglans regia* shell biomass." *International journal of environmental science and technology* 10 (2013): 231-242.
 22. M.S. Mashkour, A.F. Al-Kaim, L. M. Ahmed, and F. H. Hussein. "Zinc oxide assisted photocatalytic decolorization of Reactive Red 2 dye." *International Journal of Chemical Sciences* 9, no. 3 (2011): 969-979.
 23. S. Mahalakshmi, D. Lakshmi, and U. Menaga. "Biodegradation of different concentration of dye (Congo red dye) by using green and blue green algae." *Int J Environ Res* 9, no. 2 (2015): 735-744.
 24. A. Ökte, M.S. Resat, and Y. Inel. "Influence of hydrogen peroxide and methanol on the photocatalytic degradation of 1, 3 dihydroxybenzene." *Toxicological & Environmental Chemistry* 79, no. 3-4 (2001): 171-178.
 25. K. Tantubay, P. Das, Hydrogen peroxide assisted photocatalytic dye degradation over reduced graphene ox integrated ZnCr₂O₄ nanoparticles. *Environ. Sci. Pollut. Res.* 29, 1730917318 (2022).
 26. M.I. Mejia, J.M. Marín, G. Restrepo, L. A. Rios, C. Pulgarin, and J. Kiwi. "Preparation, testing and performance of a TiO₂/polyester photocatalyst for the degradation of gaseous methanol." *Applied Catalysis B: Environmental* 94, no. 1-2 (2010): 166-172.