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Photo-assisted Degradation of Congo red Dye using Silver Nanoparticles Synthesized by *Launaea taraxacifolia* Leaf Extract.

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Abstract

The utilization of bio-extracts in nanoparticle synthesis has emerged as a global trend. Their exceptional properties compared to bulk materials, coupled with low cytotoxicity, have established them as crucial elements in nanotechnology. This study focused on the sunlight-mediated decomposition of Congo Red dye utilising Ag nanoparticles synthesized through phytochemicals of Launaea taraxacifolia leaf extract. The sol-gel method was employed for this purpose, with the plant extract playing a pivotal role in nanoparticle fabrication. Characterization techniques such as Ultraviolet-Visible spectroscopy that showed absorbance and wavelength of 437 nm, X-ray diffraction analysis which reveals the particle size of the synthesized nanoparticles to be 22.6 nm. And Fourier Transform Infrared spectroscopy analysis which specifically revealing multiple peaks ranging from 632 to 3317 cm^{-1}. The prominent band at 1637.8 cm^{-1} indicated C–N and C–C stretching, while the band at 3317.0 cm^{-1} corresponded to stretching vibrations of O–H groups in water, alcohol, and phenols. These bio-reduced silver nanoparticles were utilized for degrading Congo red dye, known for its detrimental impact on water-dwelling creatures and the human race. Notably, absolute disintegration of the dye was achieved within 120 hours of incubation under sunlight, showcasing the nanoparticles' efficacy in water purification through photocatalytic degradation processes.

Keywords: Congo red, photo-degradation, silver nanoparticles, bio-reduced

Introduction

The expansion of economic development and urban sprawl has resulted in widespread water contamination, particularly from textile wastewater containing harmful pollutants like dyes, antibiotics, and pigments (Mirgane, Shivankar, Kotwal, Wadhawa, & Sonawale, 2021; Ariaeenejad, Motamedi, & Salekdeh, 2022). These pollutants, prevalent in discharge from textile, paper, leather, and cosmetic plants, pose serious threats to the ecosystem, soil fertility, and human wellness. The visible coloration of these pollutants, even at low concentrations, renders the water hazardous (Saravanan et al., 2021). With global population growth and ongoing industrialization, the risk of water scarcity is anticipated to rise as natural drinking water sources become increasingly unsafe. It is imperative to develop cost-effective and reliable technologies for eliminating these contaminants, ensuring the usability of water in the face of these challenges. Various methods can be employed to combat environmental pollution, and photocatalysis stands out as an efficient and eco-friendly approach with promising applications in pollution control (Javanbakht, & Mohammadian, 2021). The utilization of visible light photovoltaic (VLT) systems not only enhances the effectiveness of photocatalysis in outdoor environments but also facilitates its extension indoors, addressing limitations associated with low UV radiation. Several techniques can be employed to degrade dyes, encompassing physical, chemical, biochemical, and radiochemical methods; each having its own set of advantages and drawbacks (Al-Zaban, Mahmoud, & AlHarbi, 2021). The efficiency of these methods is influenced by various factors. Since some approaches generate secondary pollutants, it is crucial to explore alternative, more efficient, and cost-effective methods to address this persistent issue. In recent years, nanoparticles have gained popularity in wastewater removal owing to their extensive surface area, outstanding adhesion

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capabilities, swift dispersion, and rapid attainment of stability (Ariaeenejad *et al.,* 2022; Slama *et al.,* 2021). However, the physicochemical techniques utilised in nanoparticle preparation, including electro-spray and laser pyrotechnic ablation, frequently demand costly equipment, increased energy consumption, and the utilisation of toxic and hazardous chemicals, thereby presenting environmental concerns.

Recently, nanotechnology has found application in wastewater treatment, particularly through the utilisation of silver nanoparticles (AgNPs). The heightened reactivity of AgNPs, attributed to their expansive surface area, makes them effective in photocatalytic degradation. This process ensures swift pollutant removal with no polycyclic formation, ensuring a rapid and efficient approach to wastewater treatment (Somasundaram et al., 2021; Mirgane et al., 2021). Moreover, in recent developments, the successful synthesis of AgNPs has been achieved through plant-mediated methods. This approach is recognised for being both time and cost-efficient in the production of silver nanoparticles.

Before the 19th century, the primary origin of dyes was natural dyes derived from plants. However, with the advent of the mid-19th century, artificial colors emerged, leading to the gradual decline of natural dyes. The heightened utilisation of synthetic dyes since then has been associated with detrimental impacts on the environment and linked to adverse health effects in living systems.

The wide lettuce, scientifically named *Launaea taraxacifolia*, is a plant species belonging to the Asteracaea family. It is native to Africa and is commonly found in tropical and subtropical regions. This plant has a rich history of traditional use across cultures, recognized for its medicinal, pesticidal, and cosmetic qualities (Javanbakht, & Mohammadian, 2021; Yusuf, Shabbir, & Mohammad, 2017). Different components of the plant, such as leaves, find application in various fields. The *Launaea taraxacifolia* plant is highly appreciated for its earth-friendly and sustainable minded characteristics. The present research is concentrated on the synthesis of AgNPs from plant source, aiming to employ them in the degradation of synthetic dye, potentially offering a more sustainable approach.

Materials and Method

Collection and Preparation Plant Extract

Launaea taraxacifolia leaves (depicted in Fig. 1) were gathered from the Sayedero Local Market in Ilaro, Ogun State, Nigeria and was authenticated by Botanists in the Department of Science Laboratory Technology at Federal Polytechnic Ilaro, Ogun State. The leaves underwent a cleaning process using tap water followed by rinsing with dechlorinated tap water to eliminate any impurities. Subsequently, 20 g of the leaves were diced into small fragments and mixed with 100 ml of sterilized distilled water. This mixture was then subjected to boiling for 2 hours at 60°C using a water-bath, and the resulting extract was filtered through 0.6 µm filters. The extract derived from *Launaea taraxacifolia* leaves was then employed for the synthesis of AgNPs.

Figure 1: Wild lettuce (*Launaea taraxacifolia*) leaves

Preparation of Launaea taraxacifolia Leaf Extract Mediated Silver Nanoparticles (AgNPs)

The synthesis of AgNPs involved preparing a standard reaction mixture, comprising 50 ml of *Launaea taraxacifolia* leaf extract and 450 ml of 1 mM $AgNO_3$. This mixture was then subjected to microwave heating at 600 watts for 5 minutes with intermittent stirring. Afterward, it underwent incubation in a water-bath at 75°C for 12 hours. During this process, AgNPs were formed through the reduction of Ag^+ to Ag^o mediated by the *Launaea taraxacifolia* leaf extract. The generation of AgNPs was confirmed by observing the colour change in the reaction solution. Additionally, UV-visible spectrophotometric analysis was used to verify the generation of AgNPs mediated by the plant leaf extract (Osuntokun, Onwudiwe, & Ebenso, 2019; Somasundaram et al., 2021; Mirgane et al., 2021).

Optical Properties of the Synthesis Launaea taraxacifolia Leaf Extract Mediated Silver Nanoparticles (AgNPs)

The photonic absorption properties of the AgNPs were examined using a Cary 50 UV-visible spectrophotometer.

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This instrument operates at a resolution of 1 nanometer and covers a wavelength range from 200 to 800 nm.

Purification of Launaea taraxacifolia Leaf Extract Mediated Silver Nanoparticles (AgNPs)

During the purification process of nanoparticles, the reaction mixture underwent centrifugation at 5,000 rpm for 20 minutes. The resulting pellet was then rinsed with dechlorinated water and subjected to centrifugation again at 5,000 rpm for 20 minutes to obtain a clean supernatant. Following this, the washed pellet was air-dried overnight at room temperature. The dried AgNPs) were subsequently weighed and subjected to further analysis to determine their shape and size characteristics (Somasundaram *et al.*, 2021; Mirgane *et al.*, 2021).

Photocatalytic Degradation of Congo Red (CR)

The photocatalytic decomposition of Congo red (CR) dye under direct sunlight was evaluated using biosynthesized AgNPs. To start, a stock solution was made by dissolving 50 mg of CR dye in 500 ml of double-distilled water. Next, to guarantee even dispersion for catalytic degradation, 20 mg of AgNPs were introduced into 50 ml of the CR solution and stirred vigorously with a magnetic stirrer for 30 mins. Additionally, a control group devoid of AgNPs was kept. The deterioration process was then allowed to occur in the tubes holding the solutions exposed to sunshine. In order to verify total degradation, the absorption spectrum of the suspension mixture was intermittently monitored using the UV-visible spectrophotometer. In particular, the distinctive absorption peak of the CR solution in the 350–700 nm range was the focus of this monitoring (Osuntokun *et al.*, 2019; Kumari, Acharya, Naresh, Bhanja, & Kumar, 2021).

Characterisation of Synthesised Silver Nanoparticles (AgNPs)

Silver nanoparticles (AgNPs) were analyzed using robust methods such as ultraviolet-visible (UV-Vis) spectroscopy, X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, and scanning electron microscopy (SEM).

Results and Discussion

Leaf Extract Mediated Silver Nanoparticles Synthesis

Silver nanoparticles (AgNPs) were effectively synthesized using *Launaea taraxacifolia* leaf extract and 1 mM $AgNO_3$. At the outset, upon introducing 1 mM AgNO3 solution to the aqueous leaf extract, no immediate alteration in colour was noted in the reaction medium. Nevertheless, following incubation of the mixture in a water-bath at 80°C for 20 minutes, the solution's colour transitioned from colourless to dark brown, signifying the successful generation of AgNPs (Fig. 2) (Osuntokun *et al.*, 2019).

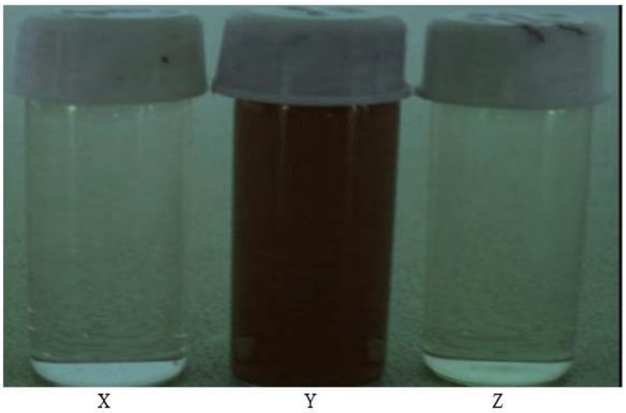

Figure 2: (X) the aqueous solution of 1mM $AgNO_3$ (Y), after addition of leaf extract at 20 mins incubation (Z*). Launaea taraxacifolia* leaf extract.

UV-Vis Spectroscopy Analysis Synthesised Silver Nanoparticles (AgNPs)

Confirming the synthesis of AgNPs involved monitoring with a UV-Vis spectrophotometer, chosen for its convenience in tracking the reduction of metal ions via surface plasmon resonance (SPR). SPR emerges from the resonant oscillation of conductive electrons at the nanoparticle interface upon exposure to incident light, leading to distinctive optical absorption spectra in the UV-visible range.

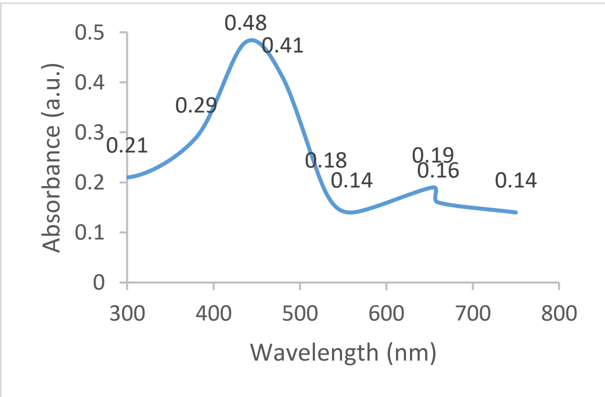

Figure 3: UV-Vis absorption spectrum of AgNPs, synthesized by *Launaea taraxacifolia* leaf extract.

This spectral analysis revealed a distinct and intense absorption band at 437 nm in the UV-Vis spectra (Fig. 3), attributed to SPR excitation, indicating the uniformity and isotropic nature of the nanoparticles. This finding aligns with prior research (Somasundaram *et al.*, 2021; Mirgane *et al.*, 2021). Interestingly, a separate study generating

AgNPs from pomegranate peel extract showed a similar UV-Vis absorption spectrum with an absorbance peak centered at 434 nm, emphasizing the consistency of UV-Vis spectroscopy in characterizing nanoparticles across different synthesis approaches and source materials (Arumugam *et al.*, 2021).

Fourier Transform Infrared Spectroscopy Analysis of Synthesised Silver Nanoparicles (AgNPs)

Silver nanoparticles (AgNPs) were subjected to *Fourier Transform Infrared* (FTIR) spectroscopy studies to identify potential compounds responsible for effectively stabilising and capping AgNPs produced using *Launaea taraxacifolia* leaf extract. Figure 2 illustrates the FTIR spectra of the stabilised AgNPs. Based on spectral analysis, the functional groups stabilized and reduced AgNPs as they transitioned into their oxidized forms. The broad peak visible at 3000 to 3500 cm⁻¹ is associated with the stretching vibrations of O–H functional groups in phenolic, alcoholic, and carboxylic acid compounds, along with amine groups that may overlap with the O–H peak.

The stretching vibrations of –C=O in the amide II band (mainly from in-plane N-H bending) were observed in the IR bands at 1631 to 1650 cm⁻¹, a significant band in protein IR spectra. Indeed, protein stabilisation of NPs may involve both amide (N-H) stretching and C=C stretching, as indicated by the peak at 1631 to 1650 cm⁻¹. The peak at 2000–2100 cm⁻¹ was attributed to flavonoids and other C–H bending in aromatic compounds present in *Launaea taraxacifolia* leaf extract. The extract compounds also exhibited a broadband at 680 to 500 cm⁻¹, attributed to the bending region of the aliphatic chain, consistent with findings from Ravichandran *et al.* (2019) and Kumari *et al.* (2021).

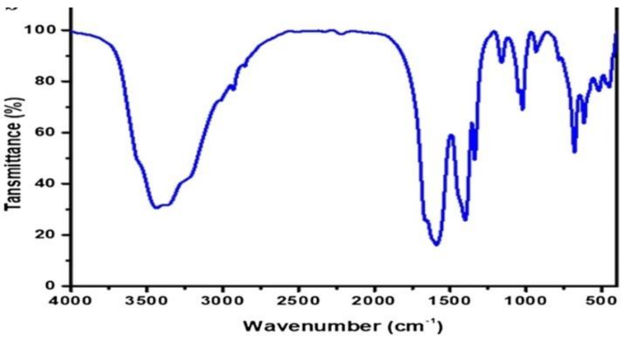

Figure 4. FTIR spectrum of silver nanoparticles (AgNPs) synthesized from *Launaea taraxacifolia* leaf extract.

X-ray Diffraction Analysis of Synthesised Silver Nanoparticles (AgNPs)

X-ray diffraction (XRD) serves as a robust analytical method used for investigating the crystalline structure of materials. By directing X-rays at a sample, interactions occur with the atoms within the material, resulting in diffraction patterns that unveil details about the arrangement of atoms within the crystal lattice.

In Figure 5, XRD patterns are presented for bio-synthesized AgNPs produced using *Launaea taraxacifolia* leaf extract. Noteworthy are the distinct diffraction peaks observed in the 111 and 200 planes at respective angles of 34.645° and 45.846°, indicating the face-centered cubic arrangement of the synthesized AgNPs across various dimensions. An additional peak at 29.268° is attributed to the crystallization of other organic compounds present in the *Launaea taraxacifolia* leaf extract. The highly intense peak observed at 34.645° corresponds to the crystalline silver. These findings validate the crystalline nature and face-centered cubic structure of the resultant AgNPs, consistent with the synthesized AgNP reference card (JCPDS Card No. 4-0783) (Kumari et al., 2021). Furthermore, the utilisation of the Debye–Scherrer equation gives an average particle size of 22.6 nm.

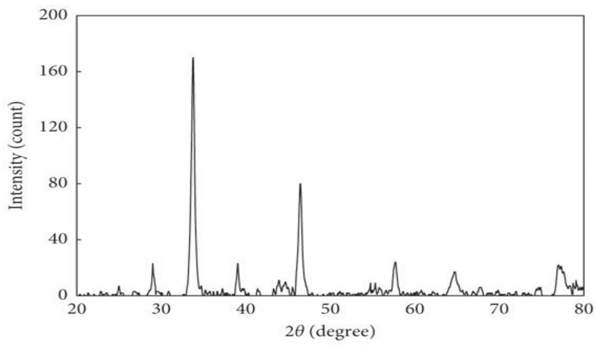

Figure 5. XRD pattern of AgNPs synthesized from *Launaea taraxacifolia* leaf extract.

Photocatalytic Degradation of Congo Red (CR)

The discharge of Congo Red (CR) dye contaminants from the textile industry poses a significant threat to water quality. Dyes, along with various organic substances, are discharged as waste, causing adverse impacts on humans and the ecosystem. CR, being a stable acidic dye with an aromatic structure, presents challenges in treatment due to its stability, high-temperature resistance, and resistance to heat and light. Hence, there is a need for effective treatment methods for CR dye. AgNPs have emerged as promising photocatalysts due to their high surface-to-volume ratio, non-toxicity, cost-effectiveness, and innovative approach to treating dye pollutants (Arumugam *et al.*, 2021).

The assessment of dye photodegradation was conducted utilising biogenically produced silver nanoparticles

(AgNPs) under sunlight exposure. As the reaction progressed, the suspension's colour faded, indicating dye degradation (Fig. 5). This degradation occurred due to light-induced generation of electron-hole pairs, enhancing reduction processes with the CR dye. UV-Vis spectrometry confirmed the degradation of CR dye through the decolourisation of the CR solution, evidenced by the decrease in absorption peak intensity at 407 nm with increasing time span (Fig. 4). The contact duration played a crucial role in dye degradation, with a linear increase observed until reaching maximum degradation after 120 hours of sunlight exposure. This improved dye elimination was attributed to the higher concentration of active sites on the AgNP surface (Al-Zaban *et al.*, 2021; Javanbakht, & Mohammadian, 2021).

Silver nanoparticles (AgNPs) synthesized from *Launaea taraxacifolia* leaf extract demonstrated efficient catalytic removal of CR dye, indicating potential efficacy in pollutant elimination, removing significant percentages of total nitrogen and chemical oxygen demand (COD). AgNPs showed a notable catalytic capacity in reducing CR dye, with their photocatalytic activity linked to surface area—smaller nanoparticles with increased coordinated Ag atoms showed enhanced dye absorption. Several parameters including light absorption, contact duration, pH, and temperature significantly influenced the photocatalytic degradation process. Moreover, the structure and size of silver nanoparticles impacted their degradation activity, with larger sizes providing more active sites and surface area for binding (Ariaeenejad *et al.*, 2022; Saravanan *et al.*, 2021).

AgNPs proved to be very potent and persistent photocatalysts within ambient settings with UV irradiation for decomposing organic compounds and dyes. It was discovered that UV radiation was particularly successful in removing dye in the presence of metal catalysts (Sosmasundaram *et al.*, 2021).

A B C D E F

Figure 6: Photocatalytic degradation of Congo red dye using *Launaea taraxacifolia* leaf extract AgNPs (a) dye alone and its subsequent degradation in sunlight. (b) 24 h (c) 48 h (d) 72 h (e) 96 h (f) 120 h

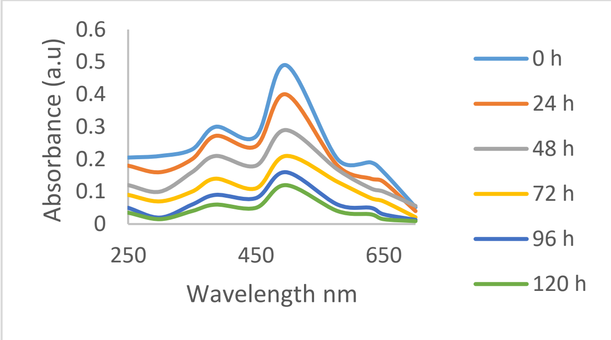

Figure 7: UV-Vis absorption spectrum of Congo red dye treated with AgNPs biosynthesized by *Launaea taraxacifolia* leaf extract at different time intervals

Conclusion

In this study, silver nanoparticle (AgNPs) were produced using *Launaea taraxacifolia* leaf extract as both capping and stabilizing agents. Incubation period at 80^{o}C, played vital role in *L. taraxacifolia* leaf extract mediated silver nanoparticles synthesis with functional groups on the surface. Crystalline structure revealed the particle size of the synthesized nanoparticles to be 22.6 nm, The nanoparticles demonstrated efficient catalytic activity in degrading Congo red dye under sunlight exposure, indicating their potential for large-scale application in eliminating hazardous dyes from contaminated water sources.

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