Green Iron (Fe) Nanoparticle Synthesis and Characterisation for Photocatalytic studies using Copper Pod Leaf Extracts

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Abstract
The uncomplicated and environmentally friendly green synthesis method that eliminates the need for hazardous chemicals, shows promise for producing nanoparticles. It is also free of solvents. In this work, the synthesis of iron nanoparticles utilising extracts from copper pod leaves is reported and their structural, functional group, morphological and elemental properties are examined. At first, the iron and organic components were visible in the X-ray diffraction pattern. The existence of iron oxide (Fe-O) stretching vibrations at 580 cm^{-1} was then verified by Fourier transform infrared analysis.

The presence of a plasma enhancement in the range of 288 to 590 nm was confirmed by the UV-visible absorbance spectrum and micrographs obtained using Scanning electron microscopy (SEM) revealed the production of irregularly shaped grains. Lastly, the effective synthesis of iron nanoparticles, employed as a catalyst for the photodegradation (~95% for 160 minutes) of methylene blue dye, was covered along with the findings.

Keywords: Green synthesis, copper pod leaf, iron nanoparticles.

Introduction
One of the most active areas of materials science research nowadays is nanotechnology. Because of their special physiochemical qualities, a variety of nanomaterials have been employed as catalysts. In the absence of a catalyst, this process is favourable thermodynamically but unfavourable kinetically. Nanoparticles, nanotubes, fullerenes and other forms of nanofibers are examples of nanomaterials. Components of nanoparticles ought to have three dimensions of no more than 100 nm[1,2]. The term "nanomaterials" refers to insoluble, biologically stable materials having an internal structure that ranges in size from 1 to 100 nm and one or more exterior dimensions. Currently, a wide range of nanoparticles including carbon, manganese oxide, copper, iron, titanium, silver, palladium and titanium, are successfully synthesised on an industrial scale.

Several researchers have reported on the green manufacturing of several kinds of nanoparticles using extract from plants. Fe nanoparticles' special qualities, such as their super paramagnetism, surface volume ratio, larger surface area and simple separation process have drawn a lot of interest. The applications of Fe nanoparticles are quite promising and include adsorbents for wastewater treatment, pigments, coatings, gas sensors, ion exchangers, magnetic data storage, magnetic recording, magnetic resonance imaging and bio-separation[3, 4]. Iron nanoparticles are known to have higher catalytic activity for the reduction and removal of dyes. The synthesis of iron nanoparticles for commercial use using plant extract has attracted a lot of attention. Iron nanoparticles are less expensive and safer [5, 6].

This work explores, the green synthesis of Ag-NPs with extracts from copper pod leaves serving as a capping and reducing agent. Using a variety of characterisation techniques, the produced sample was examined for its structural, optical, elemental, morphological and functional groups. The photocatalytic performance was finally examined in relation to the different time[7,8].

Material and Methods
Material required are filter papers, de-ionized water, ferrous sulphate ($FeSO_4.7H_2O$) and copper pod leaf. At first, de-ionized (DI) water was utilised as the solvent and ferrous sulphate was used as the source of iron. The extracts from copper pod leaves are utilised to stabilise and cap the iron (Fe) nanoparticles throughout their manufacture.

Synthesis of Nanoparticles: The fresh copper pod leaves were gathered, repeatedly cleaned in deionised water and allowed to naturally dry in the sun for a whole day. The dried copper pod leaf was then broken up into smaller pieces. Using a magnetic stirrer, 20 grams of crushed leaves were soaked for one hour at 75°C after being steeped in 200 nm deionised water. After the extracts naturally cooling, the plant residuals were filtered through Whatmann filter paper. 250 ml of the previously produced extracts were combined, at room temperature, with a 2:1 ratio of 0.1 M $FeSO_4$ to extract iron nanoparticles. $FeSO_4$ was added and a dark solution was formed indicating that the ions had been reduced. Ultimately, the sample was dried in a hot-air oven after the particulate was collected using filtration and centrifugation (4000 rpm) for 20 minutes. Ultimately, the prepared sample was calcined in a Muffle furnace for one hour at 300°C.

Characterization of Nanocatalyst: XRD (PANalytical X'Pert PRO), FTIR (FT/IR-4600 type A, JASCO), UV-Visible (Shimadzu, UV-1800) and SEM (Zeiss Fe - SEM) were used to characterise the produced nanoparticles. It was

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helpful for looking at the sample's shape, functional groups, UV absorbance. Additionally, the produced nanoparticles were utilised as a catalyst to investigate the methylene blue dye's photodegradation.

Photocatalytic Degradation: To determine the photodegradation, 25 mgs of iron nanoparticles were dispersed in 100 ml of a methylene blue dye solution at a concentration of 25 mgs/L in a 250 ml Borosil beaker. The methylene blue solution was made and kept in an absence of light for the purpose of adsorption or desorption prior to the light irradiation process. The combination solution was then exposed to visible light by being placed under UV-visible light lamps, which emit light at a wavelength of about 400 nm.

Results and Discussion

X-Ray Diffraction: The produced iron nanoparticles were examined using the X-ray diffraction technique, utilising the green synthesised approach. The range in which the XRD measurement was performed, was 2θ = 10 to 80°. Different diffraction peaks are visible, indicating the production of iron nanoparticles[9]. The origin of the broader shoulder peak at 2θ=25.84° was found to be the result of organic materials from the extracts of copper pod leaves adhering to the surface, acting as a capping and stabilising agent[10,11]. Similar peaks were observed in additional published works[12]. Furthermore, the decrease in the peak intensity of "Fe" could potentially be attributed to variations in the electron densities of the host materials, contingent on multiple factors including structure and scattering factor, among others[13,14].

Scanning Electron Microscopy: Agglomerated iron nanoparticles are visible in the Scanning electron microscopy. The artificial iron nanoparticle has an uneven form and seems to be spherical in shape. Significantly, the contact, adhesiveness and magnetic interactions between the particles cause the iron nanoparticles to clump together[15-18]. As a result, the biomolecules produced from extracts of copper pod leaves are thought to cap Fe nanoparticles and serve as stabilising agents. These biomolecules also lessened steric hindrance and electrostatic repulsion[19,20].

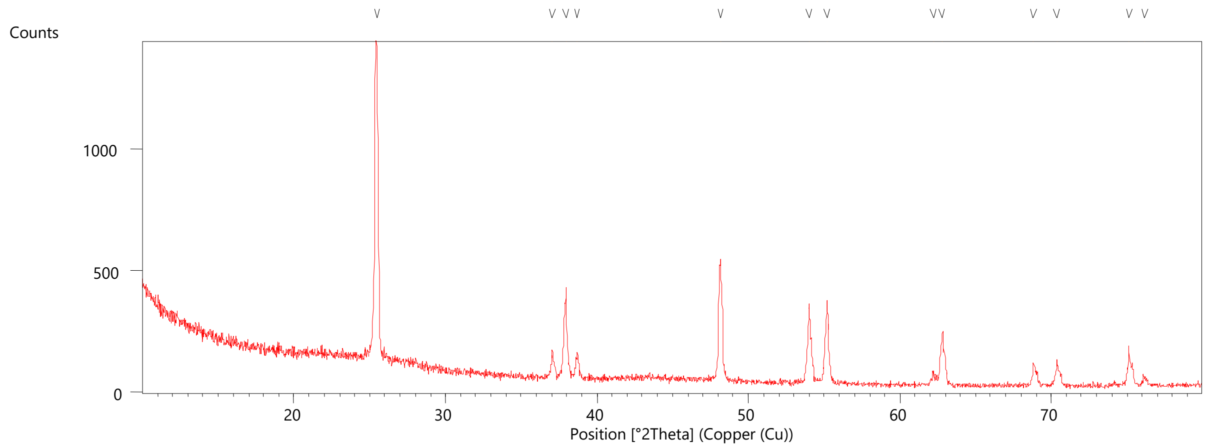

Figure 1: X-Ray diffraction

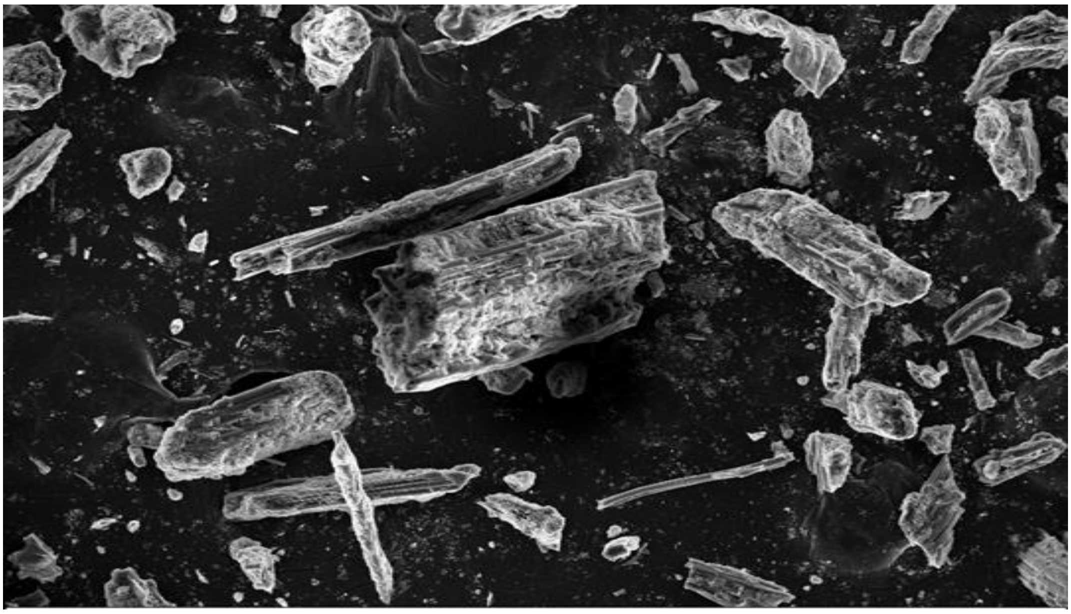

Figure 2: Scanning Electron Microscope

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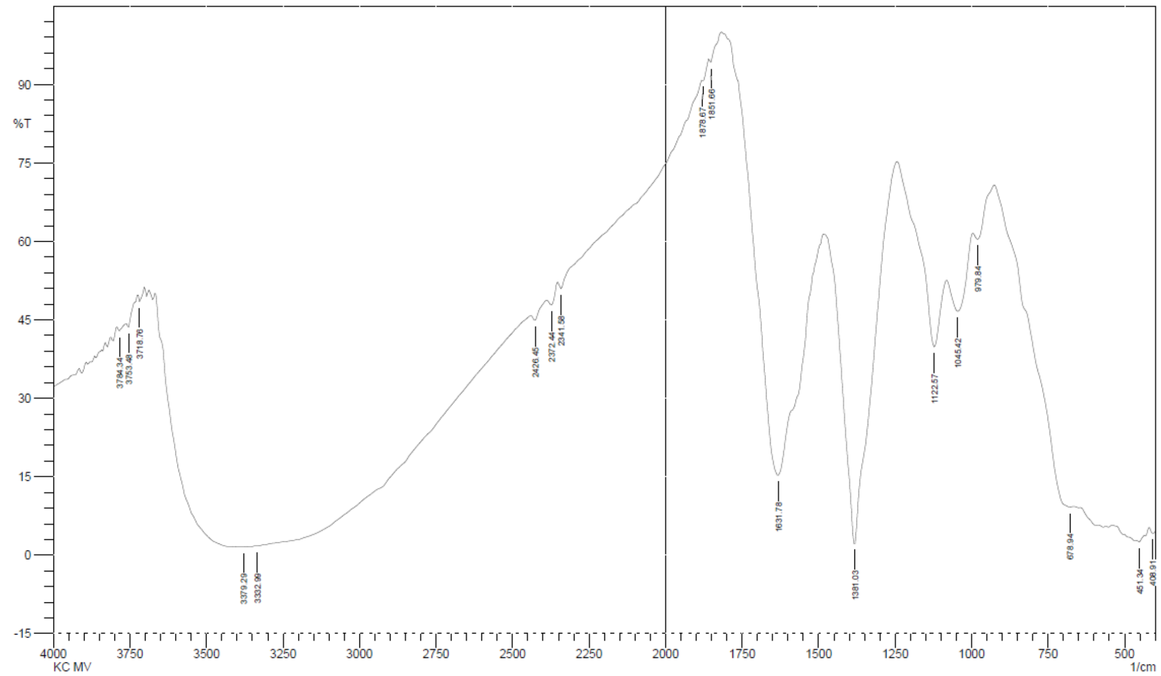

Figure 3: Fourier Transform Infrared Spectroscopy of iron nanoparticle

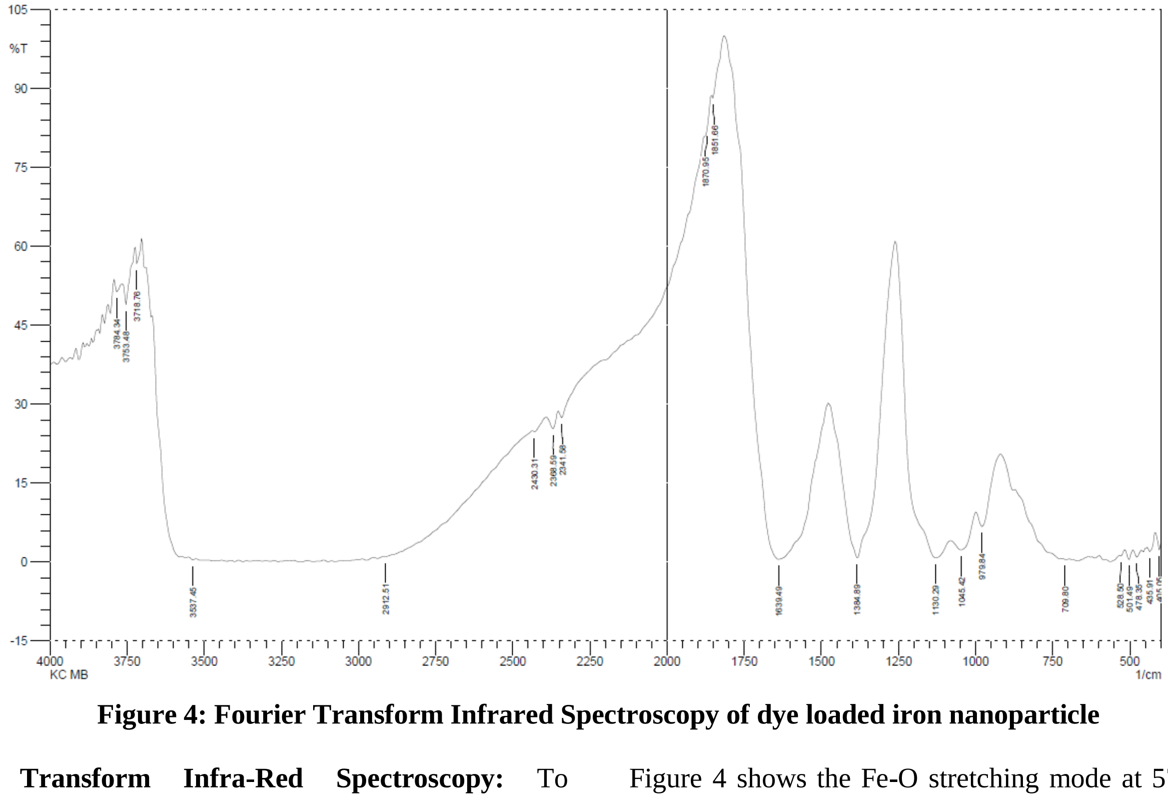

Figure 4: Fourier Transform Infrared Spectroscopy of dye loaded iron nanoparticle

Fourier Transform Infra-Red Spectroscopy: To determine the functional groups of the produced metal precursors and capping agent, Fourier transform infrared (FTIR) spectroscopic analysis was carried out plotting the FTIR transmittance spectrum in 400–4000 cm^{-1} range. This finding suggests that the copper pod extracts include a variety of functional groups, such as organic acids and polyphenols[21]. These functional groups served as a capping agent for the iron nanoparticles and were in charge of the reduction of Fe^{3+}. It is evident that the plant extract-derived synthetic Fe nanoparticles have weak transmittance peaks. Figure 4 shows the Fe-O stretching mode at 579 cm^{-1}. As seen in figure 4, the O-H stretching mode[22] is responsible for the absorption band's inception at 3485 cm^{-1}.

A band at 1699 cm^{-1} was attributed to the presence of carbonyl groups, while another band at 3000 cm^{-1} was determined to be associated to the CH and CH_2 vibration modes (aliphatic hydrocarbons)[23]. The phenolic components of the copper pod leaf extracts (C=C aromatic ring stretching vibration modes) were identified as the source of the broad band spanning from 1435 to 1599 cm^{-1}. These polyphenols

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were bonded to the iron nanoparticles and interacted with the free carboxylic groups to stabilise the material[24]. Additionally, the stretching of iron oxides can be explained by the additional band observed at $545 cm^{-1}$ [25].

Photocatalytic Performance: Iron nanoparticles were introduced to an aqueous solution of methylene blue dye in order to investigate the photocatalytic activity of green synthesised iron (Fe) nanoparticles. Additionally, constant stirring was kept up to achieve a homogenous solution. The produced solution was subjected to varying intervals of UV and visible light radiation (20, 40, 60, 80,100, 120, 140 and 160 minutes) after which the UV absorption was measured. The absorption peaks of the methylene blue dye are often found around 288 and 590 nm. The green line represents the greatest absorption and indicates a >95% improvement in photocatalytic activity[26,27].

According to reports, the SEM showed the methylene blue's nanosheet structure and 96.8% breakdown rate which is beneficial for treating wastewater[28,29]. The photocatalytic activity of iron nanoparticles demonstrated UV light irradiation with methylene blue dye. The UV-Vis absorbance was measured after the light exposure and was recorded every 20 minutes. One distinct absorption peak is visible at 290 nm, while a second, larger peak is observed between 590 and 660 nm. These peaks represent the absorption of methylene blue dye[30].

It was observed that the absorbance peaks decreased with an increase in light irradiation interval duration from 0 to 160 min. The photodegradation of methylene blue dye with iron nanoparticles is indicated by the lower absorption of UV light with increased time intervals which can be attributed to the catalytic properties of the produced dyes of the contaminated water. We also see a decrease in absorbance under UV spectrum irradiation in terms of timing and peak shifting towards the higher wavelength range. Based on the catalyst's size, our findings show that produced iron nanoparticles have a potential for photocatalytic performance.

Conclusion

In conclusion, copper pod leaf extracts were used in the green synthesis approach to create iron nanoparticles. The XRD pattern showed that the iron nanoparticles corresponding peak was located at Bragg's angle $2\theta=45.1°$. Iron stretching vibration was confirmed by FTIR. Spherical and uneven iron nanoparticles was observed in SEM micrographs. With the influence of increased time, these nanoparticles and methylene blue dye have demonstrated their superior photocatalytic ability. When exposed to ultraviolet light, the produced iron nanoparticles degraded the methylene blue dye effectively as a catalyst.

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