DEGRADATION OF DYES USING BIOLOGICALLY SYNTHESIZED IRON OXIDE NANOPARTICLES BY MANILKARA ZAPOTA LEAVES EXTRACT

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ABSTRACT
In this work, we obtained iron nanoparticles from the aqueous extract of the leaves of M. zapota and protected the environment by decreasing toxic chemicals and eliminating biological risks in biomedical applications. Different concentrations of leaf extract(0.25 g/mL, 0.125 g/mL, 0.0625 g/mL, and 0.0312 g/mL) were used and synthesized iron oxide nanoparticles. The results revealed a dependence on the particle size of Fe₂O₃ NP and synthesis conditions. The Fe₂O₃ NP samples UV–visible absorption spectra show surface plasmon (SPR) bands around 355 nm, 344 nm, 346 nm, and 344 nm at different extract concentrations. Different structural, elemental, and optical properties were analyzed by various techniques such as XRD, SEM-EDX, and FTIR. The photocatalytic activity of the produced iron nanoparticles was evaluated for the degradation of Methylene blue dye under solar irradiation. At 8 hours of exposure, green-produced iron nanoparticles efficiently destroyed the dye by almost 53.57 percent.

Keywords: Iron Oxide nanoparticles, Manilkara zapota, Phytochemicals, Dyes, Degradation.

INTRODUCTION
Nanotechnology can be involved with nanoparticle production having a precise form, dimensions, and dispersion of items when you look at the Nanoscale length and their advantages for an individual’s health. Nanometer-sized services and products possess a surface that is considerable, as well as a portion this is certainly substantial of atoms that have been studied for their special properties, such as electric, photonic, and catalytic.¹⁻³ The oxides produced by Fe₂O₃ NPs and nanocomposites substantially influence biological parameters such as antibacterial activity, drug transport, photocatalytic activity, and anticancer activity.⁴ Plant extracts are used to produce a well-characterized eco-friendly way of manufacturing nanoparticles, as various literature publications have indicated.⁵ The most common methods for making Fe₂O₃ NPs are co-precipitation, thermal decomposition, hydrothermal, sol-gel, and electrochemical.⁶ Because of their low cost, simplicity of availability, and capability to maintain other physical characteristics such as high pressure, energy, and temperature, plant extracts might be helpful as a reducing agent for producing Fe₂O₃ NPs.⁷ Polyphenolic derivatives such as flavonoids, which can function as powerful reducing agents, may be present in the aqueous leaf extracts.⁸ As a result, biodegradable plant extract compounds are chosen over pure chemical substances.⁹ Plant extracts include phytochemical components that can decrease metal salt for NP production, such as flavonoids, terpenoids, polyphenolic plant enzymes (reductases, hydrogenases, quinones), and derivatives.¹⁰⁻¹² Manilkara zapota is just a plant that belongs to the Sapotaceae household and is recognized in India as Chiku. M. zapota has long been made use of to take care of illnesses that are breathing diarrhea, rheumatism, bleeding, and ulcers. Nevertheless, using M. zapota leaves extract to synthesize Fe₂O₃ nanostructures hasn't been done prior. This research is designed to make Fe₂O₃ NPs from M. zapota.
leaves extract as a result. Dye degradation had been examined using synthesized Fe$_2$O$_3$ nanoparticles confronted with sunlight.

**EXPERIMENTAL**

**Materials**

Leaves of *M. zapota* were collected from a neighboring garden. Chemical substances such as metal precursors, polymers, etc., and solvents such as for example acetone, methanol, etc., from Sigma Aldrich, Loba, and Merck chemical substances. Whatman filter paper 12 for filtration and DI liquid ended up being made use of given that synthesis method. In this study, all compounds were of analytical quality and pure.

**Preparation of Plant Leaves Extracts**

The *M. zapota* leaves that are freshly cleansed adequately with water and washed again in double distilled water to remove the contaminants and left to air-dry for 48 h. These were dried and ground inside a ball mill until a powder that is well attained. 25 g leaf that is dry had been included to 100 mL, 200 mL, 400 mL and 800 mL of deionized water to obtain 0.25 g/mL (Sample S$_1$), 0.125 g/mL (Sample S$_2$), 0.0625 g/mL (Sample S$_3$), 0.0312 g/mL (Sample S$_4$) concentration separately. The resultant dissolutions had been sonicated at 40 °C for 30 minutes. The various extracts were allowed to cool before being filtered and stored in the refrigerator.

**Green Synthesis of Iron oxide Nanoparticles of *M. Zapota* Leaves Extracts**

2.78 gm FeSO$_4$.7H$_2$O (0.1 M) was included in 100 ml DI water and agitated for several minutes then different concentrations of leaves extract were mixed with the solution. The Iron precursor solution ended up being included with the leaf extract, and also the entire process is done at around 70 °C for 1 hour. The formation of black color in the solution reported the presence of nanoparticles, which were subsequently refrigerated until the dye degradation under solar irradiation was characterized and evaluated.

**Characterization and Applications of Fe$_2$O$_3$ NPs**

The optical characteristics uncovered by UV-Visible spectroscopy. FTIR unveiled the important points of functional groups affixed with the sample, SEM disclosed the outer lining morphology, EDX verifies the presence of metal in the sample, and the XRD method unveiled the structural analysis.

**RESULTS AND DISCUSSION**

**UV-Visible Evaluation**

Aesthetic formation of Fe$_2$O$_3$ nanoparticles oxides understood by black suggesting the synthesis of nanoparticles that has been further confirmed by double ray spectrophotometer that is UV-Visible. Figure-1 shows a consumption that is broad of Fe$_2$O$_3$ nanoparticles at different concentrations of extract (S$_1$-S$_4$) tend to be 355 nm, 344 nm, 346 nm, and 344 nm correspondingly. Due to absorption, this is certainly light scattering, ultraviolet consumption band in the variety of 330 nm–450 nm discovered for different concentrations. Earlier research yielded outcomes that are comparable. Plant polyphenols and flavonoids act as reducing agents being capping resulting in iron-oxide nanoparticle formation. The band gap energy ($E=\hbar*c/\lambda$) was revealed to be 3.49 eV, 3.60 eV, 3.58 eV, and 3.60 eV at various concentrations of extract S$_1$-S$_4$ that is respectively.

**FTIR Analysis**

The current presence of few ingredients that are phytochemicals of *M. zapota* extract at varied concentrations ended up being based on FTIR analysis. The FTIR spectra suggest a peak at 3300–3600 cm$^{-1}$ as a result of extending oscillations of the amine this is certainly the main and polyphenolic O–H groups at various doses (S$_1$-S$_4$) plant of *M. zapota*, respectively (Fig.-2). The occurrence had been demonstrated by these peaks of coumarins, alkaloids, flavonoids, and terpenoids, which are responsible for stabilizing the Fe$_2$O$_3$ NP’s. The strong band observed between 1100 and 1000 cm$^{-1}$ at concentration
extract of *M. zapota* suggests the incident for the C–N extending, the vibration of the aliphatic amines. The C–H fold of alkenes revealed between 650 cm\(^{-1}\)–1000 cm\(^{-1}\) in the spectral range of nanoparticles. The shift when you look at the bands is recognized as the participation regarding the functional categories of the various concentrations of the herb within the synthesis of Fe\(_2\)O\(_3\) nanoparticles.\(^{18,19}\)

**Fig.-1: UV–Visible Spectrum of Fe\(_2\)O\(_3\) Nanoparticles for Various Concentrations**

**Fig.-2: FTIR Analysis of Fe\(_2\)O\(_3\) Nanoparticles for Various Concentrations**

**XRD Analysis**

The iron oxide nanoparticles formation was confirmed by XRD analysis. The XRD pattern(Fig.-3) depicts the presence of the magnetite phase at various concentrations of *M. zapota* leaf extract. The diffraction at 2\(\theta\) = 29.08\(^\circ\), 28.17\(^\circ\), 28.72\(^\circ\), and 28.64\(^\circ\)at different concentrations of *M. zapota* leaf extract can be accounted for Fe\(_2\)O\(_3\), which is following the JCPDS card No.-19-0629. The narrow and crisp diffraction peaks obtained demonstrate the strong crystallinity of the produced nanoparticles.

**SEM Analysis**

SEM was used to examine the size and shape of the produced Fe\(_2\)O\(_3\) NPs. Figure-4 (a)–(d) demonstrates the generation of iron oxide nanoparticles with respect to *M. zapota* leaf extracts concentration at different magnification levels. The photos well illustrate the cubical iron-oxide nanoparticles formation which is

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spread uniformly, with bare aggregation that is minimal. The SEM disclosed the typical size of nanoparticles between 50–400 nm at different amounts of *M. zapota* leaf extract (S₁–S₄). The morphology reveals that almost all individual nanocrystals have a surface that is rough well hexagonal facets. Minor nanostructures that are irregular-shaped be viewed when you look at the photos as well.

**EDX Analysis**

Figure-5 shows the EDX spectra of biosynthesized NPs at different concentrations of *M. zapota* leaf extract. The Fe₂O₃ NPs show presence of oxygen and iron at different concentrations of *M. zapota* leaf plant, correspondingly. Weight percentages associated with Fe₂O₃ NPs with concentration are provided in Table-1 with their respective EDX data, which confirms its purity.

<table>
<thead>
<tr>
<th>Concentration (g/mL)</th>
<th>Element</th>
<th>Mass%</th>
<th>Atom%</th>
</tr>
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<tbody>
<tr>
<td>0.25</td>
<td>Fe</td>
<td>78.86</td>
<td>51.66</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>21.14</td>
<td>48.34</td>
</tr>
<tr>
<td>0.125</td>
<td>Fe</td>
<td>77.55</td>
<td>49.74</td>
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<tr>
<td></td>
<td>O</td>
<td>22.45</td>
<td>50.26</td>
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<tr>
<td>0.0625</td>
<td>Fe</td>
<td>78.40</td>
<td>50.98</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>21.60</td>
<td>49.02</td>
</tr>
<tr>
<td>0.03125</td>
<td>Fe</td>
<td>78.61</td>
<td>51.29</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>21.39</td>
<td>48.71</td>
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</tbody>
</table>

**Fig.-3: XRD Evaluation of Fe₂O₃Nanoparticles for Various Concentrations**

**Fig.-4: SEM Micrograph of Fe₂O₃Nanoparticles for Various Concentrations**
Catalytic Activity of Fe$_2$O$_3$ NPs

The dye methylene blue was used to demonstrate the photocatalytic activity of Fe$_2$O$_3$ nanoparticles on dye degradation. Methylene blue deteriorated at different durations in the visible area in the presence of Fe$_2$O$_3$ nanoparticles. The absorption spectra for methylene blue showed peaks declining for different time periods. Initially, the peaks noticed at 663 nm for methylene dye this is certainly decreasing with increasing exposure time, suggesting photocatalytic degradation of dye. The progressive drop in dye absorbance value approaching the baseline and increasing peak for Fe$_2$O$_3$ nanoparticles indicate that the photocatalytic degradation of the dyes has been completed. At 8 hours of exposure time, UV spectra illustrate a typical SPR band for iron nanoparticles as the dye concentration is reduced (Fig.-6).

![Fig.-5: EDX Pattern of Fe$_2$O$_3$ Nanoparticles for Various Concentrations](image)

![Fig.-6: MB dye degradation by Fe$_2$O$_3$ Nanoparticles for Various Concentrations](image)

At 8 hours, the degradation efficacy of Fe$_2$O$_3$ nanoparticles was measured to be 53.57 percent (shown in Table-2). The degradation portion increased as the dye Fe$_2$O$_3$ nanoparticles complex was exposed to sunlight for a more amount this is certainly extended of. The absorption peak for methylene blue dye was focused at 663 nm, which declined and finally vanished as the response time grew, recommending that the dye be eliminated.

<table>
<thead>
<tr>
<th>Exposure Time</th>
<th>% Degradation of Dye</th>
</tr>
</thead>
<tbody>
<tr>
<td>2h</td>
<td>7.34±0.30</td>
</tr>
<tr>
<td>4h</td>
<td>30.16±0.15</td>
</tr>
<tr>
<td>6h</td>
<td>40.64±0.24</td>
</tr>
<tr>
<td>8h</td>
<td>53.57±0.34</td>
</tr>
</tbody>
</table>

Table-2: MB Dye Degradation (in %) by Synthesized Iron Oxide Nanoparticles (S$_3$)
CONCLUSION
The green approach is achieving popularity because of the reduction of harmful chemicals and synthesizing of desired goods economically. Green synthesis of Fe₂O₃ nanoparticles shows a far more compatible, environmentally friendly, low-cost, and non-time-consuming strategy. Herein, the iron-oxide nanoparticles had been synthesized simply by using plant leaf extract of M. zapota at different concentrations (S₁ - S₄). The quantity and size of nanoparticles generated are extremely impacted by the concentration. SEM revealed the shape is certainly uneven of nanoparticles with sizes including 50 to 400 nm. The crystalline nature was identified by making use of XRD, and iron is elementally determined utilizing an EDX spectrum. Methylene blue dye is utilized to test the photocatalytic task of green-produced Fe₂O₃ nanoparticles. The primary absorption peak at 663 nm steadily dropped as the exposure duration increased, showing photocatalytic degradation dye. The present study discovered that utilizing an eco-friendly process to synthesize Fe₂O₃ nanoparticles has outstanding photocatalytic properties against dye molecules and can be used to treat polluted water that is contaminated with distinct dyes.

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REFERENCES