Coconut oil capped nano iron oxide for EMI shielding application

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Abstract: The super-paramagnetic particles of large surface area with controlled size Fe₂O₃ nanoparticles are synthesized by addition of reducing agents along with green capping agents via Co-precipitation method which is one of the simplest and productive method to synthesize such nanoparticles in large quantities. γ-Fe₂O₃ NPs so-obtained as confirmed by XRD were further characterized by various analytical techniques like UV-Visible, and FT-IR Spectroscopy, SEM/EDX and PSA. Nanocomposite films of very small thickness are fabricated by blending capped and uncapped Fe₂O₃ nanoparticles in PVA matrix at different loading concentration and their shielding efficiency is studied using Vector Network Analyzer (VNA) in the X-band frequency (8.2-12.4 GHz) and Kₐ-band frequency (12.4-18 GHz). EMI SE in Kₐ-band was maximum for capped Fe₂O₃ NPs PVA film with value of -13.06 dB, better than uncapped Fe₂O₃ NPs/PVA film.

Key words: Green surfactant, nano-particles, polymer composites, EMI shielding

1. Introduction: Recently magnetic nanoparticles are in great demand due to their unique properties such as paramagnetic behavior, have highly magnetic sensitivity, high coerciveness etc. They are preferred in a very wide range of fields including magnetic fluids, data storage techniques, catalysis, and biomedical applications [1]. In the last decade, several types of iron oxide nanoparticles were investigated viz; magnetite (Fe₃O₄), ferromagnetic and/or superparamagnetic at <15 nm (Fe⁸nFe³m₂O₄), hematite (α-Fe₂O₃), maghemite (γ-Fe₂O₃), wüstite, antiferromagnetic (FeO), ε-Fe₂O₃ and β-Fe₂O₃. Such nano-particles due to exposure to air, can get oxidized resulting in loss of magnetism and dispersability. A comparison between two important iron oxide nanoparticles, maghemite (γ-Fe₂O₃) and magnetite (Fe₃O₄) has been well documented [2]. Size, shape, surface chemistry and the application of nanoparticle is dependent on the preparation method and thus has always been a challenging task for chemists and materials scientists. A large variety of chemical route have attracted researchers e.g. co-precipitation, microemulsion, hydrothermal, sonochemical, and thermal decomposition etc. Co-precipitation is the one of the most popular methods in terms of economics and commercial production [2-4]. Despite several advantages that co-precipitation suffers by often compromising the particles size distribution. To, overcome such drawbacks many research groups reported modifications and improvements. Ahn et al [3] suggested the stoichiometric ratio of iron salts Fe²⁺, Fe³⁺ as 1:2 with the addition of ammonia solution [NH₃ (aq)] by varying pH from 1.5 to 11.0 at 25°C. Kim et al [5] proposed synthesis of superparamagnetic monodispersed iron oxide NPs by co-precipitation with ferric chloride hexahydrate under N₂ atmosphere. Morales [6] differentiated between α-Fe₂O₃ and γ-Fe₂O₃ using the co-precipitation
method and single precursor of Fe (III) salt and drop wise addition of NaOH solution. Lee et al [7] introduced another method called piezoelectric nozzle method for synthesizing maghemite particles where the reducing agent hydrochloric acid (HCl) is added through pipette nozzle to prepare particles of size 3 to 8 nm. The above methods preferred only conducting the reaction in nitrogen atmosphere to obtain only maghemite particles, in alkaline pH and high temperature in the range of 75 °C – 90 °C. The introduction of capping agent further controls the size of particles. Morales et al [6] carried out the reaction using polyvinyl alcohol (PVA) as surfactant to obtain smaller particles. Budhwar et al [8] employed coconut oil as surfactant by adapting reported method of co-precipitation and their modification particles with surface area of 45.65 m²/g can be synthesized easily. The availability of various size, shaped and morphology of iron oxide, wide application potential has been documented in electrical, magnetic and electronic devices. Iron oxide has special place of application when it comes to electronic devices including safety from electromagnetic radiation.

In the era of technology, humans are connected deeply with modern communication devices such as mobile phones, radios, laptops, television etc. With the ever increasing use and number of electronic devices in almost all areas that human might cover, the harmful effects of also increases due radiation. All the electronic devices either absorb or radiate electromagnetic (EM) waves and affect the performance of other devices or electronic circuits thereby creates interference [9]. Thus EM interference (EMI) has become one of the major issues. Multifunctional and light weight EMI shielding composite materials are required to minimize EM interference to offer better shield for humans to avoid health hazards.

Based on the understanding from the literature, it is realized that the research is mainly focused in developing EMI shielding in both X (8 – 12 GHz) and Ku-bands (12 – 18 GHz), for applications in a variety of devices/fields. Conventionally many metal based shields were used due to their firmness and corrodirbility but they were eventually substituted by polymers for want of flexible, lightweight, anti-corrosive and cost-effective materials. Polymers are being widely used in many applications including sensors, capacitors, circuits, batteries etc. Amongst them Polyvinyl alcohol (PVA) and Poly (methyl methacrylate) (PMMA) are the most preferred non-conducting polymers due to their due to their high breakdown strength, reproducibility, popularity and versatility. PVA is often more preferred because it does not react with other chemicals, provides a flexibility and durability while casting and is compatible with wide range of fillers in addition to its ability to tolerate reasonable temperature range. An effective EMI shield is dominated by three main functions: reflection, absorption and multiple internal reflections. On the surface of shielding materials usually reflection occurs because the incoming EM waves are interacting with surface mobile charge carriers. Absorption occurs when radiation interacts with electrical or magnetic dipoles of shielding material and the absorbed radiation turns into heat energy. Both reflection and absorption of shielding material depends on the high electrical conductivity. Thus, EMI shield has to be thick enough to dissipate more radiation [10-14].
There comes another term into spotlight, EMI shielding efficiency (EMI SE). EMI SE is the ability of material to attenuate the EM wave strength, defined as the logarithm of incoming power ($P_i$) to transmitted power ($P_t$) in the units of decibels (dB). The total EMI SE ($SE_T$) is the function of reflection ($SE_R$) and absorption ($SE_A$) and can be written as -

$$SE_T = SE_R + SE_A$$

where the coefficient of reflection (R), transmission (T) and absorption (A) were calculated using S parameters $S_{11}$ and $S_{21}$ or $S_{12}$ and $S_{22}$ according to following equations [9]:

$$SE_R = 10\log \left( \frac{1}{1-R} \right) = 10\log \left( \frac{1}{1-|S_{11}|^2} \right)$$

$$SE_A = 10\log \left( \frac{1}{1-A_{eff}} \right) = 10\log \left( \frac{1-|S_{11}|^2}{|S_{22}|^2} \right)$$

The commonly used nanofillers are metal such as iron, aluminum, silver, carbon and its various forms, graphenes, metal oxides, composite of different nanofillers etc. Conducting materials are preferred over semiconducting materials due to low resistivity. It is reported that ferric oxide ($Fe_2O_3$)/reduced graphene oxide (rGO)/polydimethylsiloxane (PDMS) composite with 10 mm thickness can be an effective EMI shield with efficiency of 35.83 dB which can be reduced to 23.69 dB for a 2 mm thickness at 10 wt. % of $Fe_2O_3$ loading [9]. Adapting same methodology, PVC/PMMA/GeO$_2$ nanocomposite film at 10 wt. % of GeO$_2$ loading was studied for shielding efficiency at X-band, having efficiency of 17.14 dB. When the same composite film was studied in the K$_u$-band (12 - 18 GHz), the maximum shielding efficiency of 15.423 dB was observed [16]. Iron oxide included 30 wt. % NiFe$_2$O$_4$ nanoparticles filled BaTiO$_3$ ceramics has been reported to have shown EMI shielding efficiency of more than 34 dB in the whole X-band [17]. Similarly, EMI SE of PS/TGO/Fe$_3$O$_4$ hybrid nanocomposite showed more than 30 dB in X-band.
band due to the reflectance loss by magnetic particles and absorption by TGO in polystyrene composites. [18], Presence of magnetic Co/Ni particles with SWCNTs shield of thickness 1.5 mm resulted in good shielding efficiency of 24 dB in K\textsubscript{u}-band [19]. It is also reported that the nanocomposite derived from polypyrrole and magnetic Co nanoparticles with film thickness of 2 mm showed EMI shielding efficiency (SE) of 33 dB in the K\textsubscript{u}-band. It is therefore appropriate to consider that magnetic particles in nanocomposite films may be better suited for shielding effectiveness and the efficiency can be altered by changing the particles concentration, nature and film thickness [20]. In comparison of hybrid nanocomposite films with magnetic and non-magnetic metal or metal oxides, the magnetic ones are reported to give maximum shielding efficiency [21]. It is therefore possible to conclude that magnetic nanoparticles especially iron oxide show significant increment and better shielding performance in any hybrid or nanocomposite film combinations. The effort in this article is presented for simplicity of nanoparticle synthesis as well as developing its composite with PVA with mild shielding efficiency.

2. Experimental procedure:

2.1 Materials and methods:

Synthesis of Iron Oxide NPs: Ferrous sulphate heptahydrate (FeSO\textsubscript{4}.7H\textsubscript{2}O) from SRL chemicals, Ferric chloride (FeCl\textsubscript{3}) from Sigma-Aldrich, Ammonia solution (NH\textsubscript{3})\textsubscript{aq} from SRL chemicals, Coconut Oil from local market, Ethanol (absolute) from Analytical Reagents, N-Heptane (95 %) from SRL chemicals, Acetone (CH\textsubscript{3})\textsubscript{2}CO from Fischer Scientific, De-ionized water (18.2 M\textOmega\ resistivity). For casting of EMI shield: γ-Iron Oxide NPs, Polyvinylalcohol (MW 125000, degree of polymerization 1700 - 1800) from Kemphasol, Chloroform HPLC grade (> 99.5 %) from Sigma-Aldrich, were used. Fourier Transform-Infrared spectrometer in the wavenumber range of 400 - 4000 cm\textsuperscript{-1} (Perkin Elmer Spectrum-Two) was used to obtain transmittance spectra and Ultraviolet-Visible spectrophotometer (Specord 210) was used to measure the absorbance and band gap in the wavelength range of 200-800 nm, X-Ray patterns were measured on Bruker D8 advance XRD at wavelength 1.54 Å along with scanning speed of 2° min\textsuperscript{-1}, surface morphology and % composition of elements were obtained from Scanning Electron Microscopy (ZEISS Gemini SEM) and Energy Dispersive X-Ray (EDX), particle size distribution profile was obtained using Particle Size Analyzer (PSA) (NanophoxSympa TC) and Vibrating Sample Magnetometer (VSM) was used for magnetization property of γ-Fe\textsubscript{2}O\textsubscript{3} NPs at room temperature (LakeShore Vibrating Sample Magnetometer Model 7404). Shielding effectiveness or efficiency of γ-Fe\textsubscript{2}O\textsubscript{3} NPs doped PVA films in X-band and K\textsubscript{u}-band were measured using Vector Network Analyzer (PNA Network Analyzer N5222A) at room temperature.

2.2 Synthesis of nano-particles and film preparation:

2.2.1 Synthesis of Iron oxide nanoparticles: Fe\textsubscript{2}O\textsubscript{3} NPs were made by co-precipitation method with FeCl\textsubscript{3} and FeSO\textsubscript{4} in the ratio (3:2) in de-ionized water taken in two-neck round bottom flask. The solution mixture was heated at 80 - 90°C under nitrogen atmosphere with continuous stirring throughout. Few drops of coconut oil were added as surfactant/capping agent before the addition of reducing agent. Ammonia solution was added as reducing agent until the pH of solution mixture reached the range of 9 - 14 or basic. The reaction was carried out for 4 - 5 hours at the same condition followed by cooling. The reaction was quenched with n-heptane and ethanol. The precipitate was centrifuged and washed with ethanol and acetone. The separated particles were dried out in hot air oven at 50°C overnight. The particles were crushed into fine powder and stored.

2.2.2 Casting of EMI shield: EMI shields of three different particle loading were made by impregnating with Fe\textsubscript{2}O\textsubscript{3} NPs in poly vinyl alcohol (PVA) in 1:0.1; 1:0.5 and 1:1 w/w ratio. Typically, 1.0 gm of PVA was taken in the beaker containing a few mL of chloroform and heated the mixture to form clear solution. 0.1 gm of γ-Fe\textsubscript{2}O\textsubscript{3} nanoparticle was separately taken in few mL of chloroform or
ethanol and sonicated for dispersion and then added to PVA solution (A10). The completely blended solution was poured onto a mould and was allowed to dry until the chloroform evaporates and was left overnight, leaving a film of Fe$_2$O$_3$/PVA nanocomposite. The final dried film was peeled out of the mould. Similar procedure was practiced for preparation of 1:0.5 (A50) and 1:1 (A100) film. Another film was also made with 1:1w/w of uncapped γ-Fe$_2$O$_3$ NPs and PVA (A00) to study the EMI shielding effectiveness for comparison (Figure 2B).

3. Results and discussions:

Synthesis of iron oxide nano-particles in the present work was done using green surfactant as per the reported protocol [8]. According to the possible steps for synthesis, the salts were taken in a beaker and mixed with a few drops of coconut oil for controlling the particle growth and nucleation process. The oil rich in carboxylic groups will offer effective surface capping to the particles. It is well documented that coconut oil containing a several fatty acids and the main component is lauric acid. Thus it is believed that iron lauriate or other such complex will be forming as intermediate complex during the synthesis which eventually breaks down to generate iron oxide capped with fatty acid. The overall formation of the nano-particles and their loading in polymer for casting the film is presented in Figure 2A and 2B. The as-prepared nano-particles were characterized by various spectroscopic tools before using them for casting the film.

The absorbance and band gap for the samples are obtained from UV-Visible spectroscopy measurement in the range of 300 - 800 nm (figure 3). The maximum absorption observed was approximately between 575 - 580 nm and the corresponding band gap was estimated to be in the range of 2.1 - 2.2 eV. As a result of small sized particle formation, blue shift with respect to bulk band gap energy value (~ 2 eV), was observed. The band-gap of iron oxide may vary depending on the phases (α, β, and γ). The presence of capping agent resulted in excellent size control of particle. The consistency in absorption value indicated that iron oxide NPs with controlled size homogeneous size distribution with broad absorption profile was formed in all preparations.

Figure (2): A) Synthesis of Fe$_2$O$_3$ NPs and B) Casting of EMI Shield/Film.
Figure (3): UV-Visible spectra of as-prepared Fe$_2$O$_3$ NPs.

FTIR spectrum (Figure 4a) showed broad peaks at 550 cm$^{-1}$, 1100 cm$^{-1}$ and 1434 cm$^{-1}$ for stretching vibrations of metal-oxygen (Fe-O) and matched well with literature reports however, presence of other phases may not be ruled out [8]. The spectra of Fe$_2$O$_3$ NPs and PVA exhibit a combination of various bonds, deformation, stretching and vibrations. The dominance of Fe-O bond is observed from characteristic peak at about 600 cm$^{-1}$. The other low intensity peaks are considered due to C-O stretching and $-\text{CH}_2$ deformation, $-\text{C-OH}$ stretching and $\gamma$(C-H) vibration respectively.

Figure (4): (a) Typical FT-IR Spectra of Fe$_2$O$_3$ NP sample (b) 1:1 w/w loading in PVA (A100).
The peaks between 2100 cm\(^{-1}\) to 2400 cm\(^{-1}\) attributes to –CH\(_3\)-CH\(_2\) stretching and C-H stretching respectively. These distinct peaks show the intermolecular relation between polymers and nanofillers in the nanocomposite films. Typically all composite films showed similar IR pattern, but since sample A3 was loaded to PVA and various loading of the samples were analyzed by IR therefore IR of A3 and of 1:1 composite film is presented in Figure (4).

The characteristic broad peaks observed from the XRD plot matches (figure 5) with the literature values of γ-Fe\(_2\)O\(_3\) NPs in the samples [8, 15]. The peaks in the range of 2θ (degree) of 30, 35, 43, 57, 63 was observed due to diffraction from 211, 220, 311, 400, 511 and 440 crystal planes of γ-Fe\(_2\)O\(_3\). The average crystallite size (D) was estimated by Scherrer’s equation. The D values obtained for 311 crystal plan about 15 nm. The crystal structure, the crystallite size (D) and interplanar spacing (d) matched well with the literature values [15]. A typical XRD pattern of is presented below:

![XRD pattern of γ-Fe\(_2\)O\(_3\) NPs](image)

**Figure (5):** XRD pattern of γ-Fe\(_2\)O\(_3\) NPs.

Figure (6) shows the SEM images of one of the samples. It is observed that the iron oxide NPs are spherical in shape albeit not without agglomeration. The formation of clusters of controlled size can be a because of the presence of capping agent in the reaction. The EDX/EDS studies are conducted to investigate the composition of each element in the sample. For a typical sample A3 (Figure 6), the elemental composition obtained showed strong peaks of Fe and O. The weight composition of Fe and O is obtained as 58.59 % and 31.69 % respectively. The remaining weight % is observed due to the presence of C and N in from the capping agent and reducing agent. (Table 1).

The particle size distribution analysis was done to understand the distribution of the particles in a given sample after dispersion in a suitable solvent. Since the particles can undergo cluster formation, unit dispersion is ensured before analyzing particle size. Figure (7) shows the particle size distribution profile. The distribution varied in the range of about 5 - 25 nm and the average size obtained for the particle was about 10 nm indicating reasonable narrow distribution.
The magnetization curve was plotted within -1T and +1T emu/g and the magnetic behavior of particles can be studied from this plot. The increment of the plot is showing about the paramagnetic behavior of sample in the positive direction. The magnetic flux density was observed to be increasing with magnetic field and gets saturated beyond the field intensity of 5500 G and the saturation was obtained in the range
of 0.9 to 1 emu/g. The curve indicate the low coercivity and moderate saturation magnetization of the nano-particles (Figure 8).

The results indicate near superparamagnetic nature of the nano-particles, thus making these nanoparticles useful candidates for EMI shielding application because of possibility of relaxation mechanism occurring at higher frequencies. It has been studied that the magnetization saturation decreases when the magnetic particles are incorporated with non-magnetic polymer matrix and thus shielding efficiency has also been documented [10]. The purpose of magnetic particles in shielding application is its property to absorb or reflect magnetic part of the EM wave. It is also reported that magnetic behavior can offer corrosion resistance [22].

![Magnetization curve of nanoparticle.](image)

Figure (8): Magnetization curve of nanoparticle.

The VNA analysis conducted in X-band and K_u-band giving better information about the dielectric properties and shielding effectiveness of any nanocomposite films. The X-band of frequency from 8.2 to 12.4 GHz is selected because most of the electronic components emit EM radiations in this frequency range and satellite communications interference are coming in K_u-band of frequency 12.4 to 18 GHz. In the current study, the EMI shield shows poor efficiency in lower frequency but as the frequency enhances, the effectiveness also enhanced. Since the total shielding efficiency is the cumulative effect of reflection and absorption, the dominancy of absorption phenomena of EM waves is studied from the above plotted graph. It is observed that in the shield/film enriched with NPs, shielding effectiveness increases with increase in particle concentration. The EMI shielding effectiveness (EMI SE) of capped Fe_2O_3/PVA nanocomposite films of ratio (w/w) 0.1:1; 0.5:1 and 1:1 in X-band is obtained as -0.38, -0.49 and -1.94 dB respectively (Figure 9a-b). The uncapped Fe_2O_3/PVA nanocomposite films showed moderate shielding efficiency of -3.45 dB in the X-band for film with 1:1 ratio.
Figure (9): EMI shielding performance in X-band of nanocomposite films
(a) A00 (b) A10 (c) A50 (d) A100.

However, the EMI shielding effectiveness of nanocomposite films A00, A10, A50 and A100 in K_u-band is obtained as -10.39, -7.70, -9.29 and -13.06 dB respectively (Figure 10a-d). During the dipole polarization, large amount of energy is dissipated and this paves the way to maximum absorption of EM waves under varying EM field. Thus capped Fe_2O_3 NPs containing PVA nanocomposite films with 1:1 ratio can be considered as an eco-friendly efficient way to protect electronic gadgets from EM pollution. The data are presented in Table (2) and their graphical reflection is presented in Figure (11).
Figure (10): EMI shielding performance of films in K$_u$-band (a) A00 (b) A10 (c) A50 (d) A100.

Table (2): Compilation of EMI SE of nanocomposite films in X-band and K$_u$-band.

<table>
<thead>
<tr>
<th>Frequency Bands</th>
<th>Wt. % of capped Fe$_2$O$_3$ in PVA</th>
<th>Wt. % of uncapped Fe$_2$O$_3$ in PVA</th>
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<tbody>
<tr>
<td></td>
<td>A10 (1:0.1)</td>
<td>A50(1:0.5)</td>
</tr>
<tr>
<td></td>
<td>A100(1:1)</td>
<td>A00(1:1)</td>
</tr>
<tr>
<td>Max Shielding effectiveness of sample films</td>
<td>A10</td>
<td>A50</td>
</tr>
<tr>
<td>X-band</td>
<td>-0.38</td>
<td>-0.49</td>
</tr>
<tr>
<td>K$_u$-band</td>
<td>-7.70</td>
<td>-9.29</td>
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4. Conclusions: Stable super paramagnetic Fe$_2$O$_3$ NPs are synthesized using coconut oil under nitrogen atmosphere. The experiments were carried out at moderate temperature of about 90 °C, in alkaline pH employing ammonia solution. Formation of Fe$_2$O$_3$ NPs was confirmed by characterization techniques like UV-Visible, FT-IR, XRD, SEM/EDX. Polymer nanocomposite films of less than 1 mm were fabricated with various ratios viz; 1:0.1, 1:0.5 and 1:1 w/w (PVA: NPs) for capped Fe$_2$O$_3$ NPs and 1:1 w/w for uncapped γ-Fe$_2$O$_3$ NPs and EMI shielding efficiency was measured using VNA instrument in X-band and K$_u$-band. As the concentration of nano-particle increases, the absorption of EM waves enhances and thereby increases the shielding efficiency. Uncapped Fe$_2$O$_3$ NPs loaded nanocomposite shield showed maximum efficiency of -3.45 dB however, the capped Fe$_2$O$_3$ NPs containing films showed efficiency of only 1.94 dB in X-band. EMI SE in K$_u$-band was maximum for capped Fe$_2$O$_3$ NPs based nanocomposite film with value of -13.06 dB which was higher than uncapped Fe$_2$O$_3$ NPs containing nanocomposite film with the efficiency of -10.39 dB.

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