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Synthesis of Iron Oxide Nano Particles by the Use of Osmanthus Fragrance Leaf Extract

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Abstract: ***In this study, a one-pot eco-friendly synthesis technique was successfully employed in synthesizing iron oxide (Fe_3O_4) nanoparticles from $FeCl_3.6H_2O$ and $FeCl_2.4H_2O$ by the use of aqueous extract of sweet scented Osmanthus leaf. The synthesized nanoparticles were characterized by Scanning Electron Microscope (SEM), Fourier Transform Infrared, Thermogravimetry analysis (TGA), UV-vis spectrophotometer, X-ray diffraction (XRD) and Zetasizer nano 3600. The XRD analysis exhibited peaks at; 30.20°, 35.57°, 43.26°, 53.29°, 57.26°, 62.62°, 68.27° and 74.49° corresponding to 220, 331, 400, 422, 551, 440, 533 and 553 respectively which indicates the inverse spinel structure of Fe_3O_4 shows the crystalinity and high purity of our synthesized Fe_3O_4 nanoparticles. The iron oxide nanoparticles were in the size range of 20.25nm to 27.04nm.***

Keywords: Osmanthus fragrance leaf extract, Fe_3O_4, nanoparticles, synthesis, Fourier Transform Infrared Spectroscopy.

1. Introduction

Nanotechnology has attracted many scientist and engineers because of the unique properties of nano-materials such as; high surface area to volume ratio which have made them applicable in different fields such as Nano-materials are materials whose all or part of their dimension is less than 100nm, they include, nano particles, nanotubes, nano-prisms, nano-rods, nano-cubes, nano-ribbons, etc. Nano-materials have a wide variety of applications in diverse fields such as, electrons, waste water treatment, chemistry, food packaging, optics, biomedical, textiles, material science, optics, aerospace, etc. There are two routes to the synthesis of nano particles which are; top-down method and bottom-up method. The top-down method involves the use of bulk materials as the starting material (precursor) via the application of mechanical force, laser ablation, chemical energy, etc., while bottom-up consist the formation of nano particles from atoms to nuclei and nuclei to nano particles by the use of chemicals or bio-chemicals.[1-3]

Chemical synthesis of nano particles uses some chemicals that are toxic hence leading to environmental pollution so therefore, there is need for the use of green and ecofriendly approaches in making nano particles. The synthesis nano particles via green method is also known as biosynthesis of nano particles, it involves using plant extracts, fruits, biopolymers like sodium alignate, glucose, micro-organisms like fungi, yeast, bacteria, etc. in making nanoparticles [4]. Several metallic nano particles have been synthesized using green synthesis method from diverse metals and/or metals such as; examples are silver nano particles[5], zinc oxide nano particles[6], gold [7], platinum [8], nickel [9], copper nano particles[10], titanium dioxide nano particles[11] iron oxide nano particles[12], etc.

Sweet scented osmanthus is (*Osmanthus fragrans*) is a vital ornamental plant.it is an evergreen green tree that is native to Asia. It belongs to the family of Oleaceae. Sweet osmanthus flowers are used as natural and functional food flavour additives. Furthermore, they also have prospective medicinal value as a result of their good scent and biological properties. Osmanthus tea has been used in traditional Chinese medicine as a herbal tea to treat irregular menstruation, extracts of dried flowers of sweet scented osmanthus have exhibited antioxidative, neuroprotective and free-radical scavenging properties invitro [13, 14]. Sweet scented Osmanthus has phytochemicals, flavonoids, melanin, anti-oxidants, aroma active compounds, volatile compounds, etc. The flowers are employed in making, food, beverages, teas, etc. The volatile

compounds of Osmanthus include;*trans*-β-Ionone, *trans*-linalool oxide, linalool, dihydro-β-ionone, *cis*-linalool oxide, β-myrcene, γ-decalactone, *trans*-β-ocimene, etc. Aroma active compounds found in osnmanthus are; *cis*-3-hexenyl butanoate, hexyl butanoate, *cis*-β-ocimene, *trans*-β-ocimene, D-limonene, *trans*-linalool oxide, α-ionone, *cis*-linalol oxide (pyranoid), *trans*-β-ionone, *cis*-linalool oxide, allo-ocimene, linalool, neo-allo-ocimene, etc [15-20].

There are eight iron oxides that are in existence out of which hematite, magnetite and maghemite are of very significant importance and has diverse potential applications. Hematite (α-Fe_2O_3) is the most stable iron oxide. It is broadly used in gas sensors, catalyst and pigments as a result of its high corrosion resistance and low cost. It can also be used as the precursor for the synthesis of magnetite and maghemite.[21]Magnetite (Fe_3O_4) has a face centered cubic inverse spinel structure that is made of a close packed cubic array of oxide ions, where all of the Fe^{2+} ions inhabit half of the octahedral sites and the Fe^{3+} are divided equally through the continuing octahedral sites and the tetrahedral sites. [22]. Maghemite (γ-Fe_2O_3) can be called fully oxidized [23, 24]magnetite because each unit is made up of 32 O^{2-} ions, 21⅓ Fe^{3+} ions and 2⅓ vacancies and the oxygen anions result in close packed cubic array while the ferric ions are distributed over tetrahydral and octahedral sites.[25]

Iron oxide nano particles have received a lot of attentions because of their potential applications in Ferro fluids, targeted drug delivery, magnetic storage devices, tissue repair, environmental remediation, magnetic imaging, cancer treatment, sensors, cell sorting, antibacterial activity, etc. [26-29]. Iron oxide nano particles have been produced by diverse techniques using chemical and physical methods but these methods have some drawbacks examples, the use of elevated pressure, the use of toxic chemicals, the use of elevated temperature, etc. hence, there is need to overcome these limitations. Biosynthesis method was invented to eliminate the setbacks of chemical and physical synthesis methods. Biosynthesis of iron oxide nano particles involves the use of non-toxic, ecofriendly materials. Iron oxide nano particles have been biosynthesized using plant extracts, fruits, naturally derived polymers, etc. [30-33].

Green synthesis of iron oxide nanopartcles is the process that involves the use of fungi, plant extracts, biopolymers, bacteria, yeast, algae, etc. in fabricating iron oxide nano particles. Some researchers have synthesized iron oxide nano particles by using biosynthesis. [34, 35]

2. Experimental Details

2.1 Materials and Methods

Iron (3) chloride hexahydrate ($FeCl_3.6H_2O$), iron (2) chloride tetrahydrate ($FeCl_2.4H_2O$) and sodium hydroxide (NaOH) were purchased Sinopharm Chemical Reagent Co. Ltd. Beijing China. Fresh leaves of sweet scented Osmanthus were picked from Wuhan Textile University Sunshine Campus.

2.2 Preparation of Leaf Extract

Figure 1 illustrates the schematic process of making our iron oxide nano particles. Fresh leaves of Osmanthus picked from the tree were thoroughly washed with running tap water, then rinsed very well with double distilled water, shade dried for 10 days, grinded with a dry blender, sieved with a sieve and stored for use later use. 3 grams of the dry leaves was weighed and put in a beaker having 50ml of distilled water and put in a water bath with constant magnetic stirring at 60^{o}C for 13 minutes, then removed from the water bath allowed to cool to room temperature and filtered using Whatman no. 1 filter paper to obtain Osmanthus leaf extract. 1 filter paper to get citrus reticulata leaf extract which was stored at 4^{o}C for further use.

2.3 Synthesis of Iron Oxide nano particles

The iron oxide nano particles were prepared as shown in figure 1.$FeCl_3.6H_2O$ and $FeCl_2.4H_2O$ were dissolved individually in double distilled water in the mole ratio of 2:1 respectively at room temperature. The Fe^{3+} solution was added into the Fe^{2+} to get the Fe^{3+}/ Fe^{2+} solution. Citrus reticulate extract was added to the iron salt solution, then, freshly prepared sodium hydroxide solution (3mol/L) was added drop-wise under constant magnetic stirring at 80^{O}C to adjust the pH to 11. The solution was kept for 1 hour under magnetic stirring in an inert environment under nitrogen atmosphere in order to avoid the oxidation of the nano particles. The reaction mixture was decanted after 1 hour by the use of magnetic decantation to get black iron oxide (Fe_3O_4) nano particles which were washed with double distilled water several times and vacuum dried at 60^{O}C .

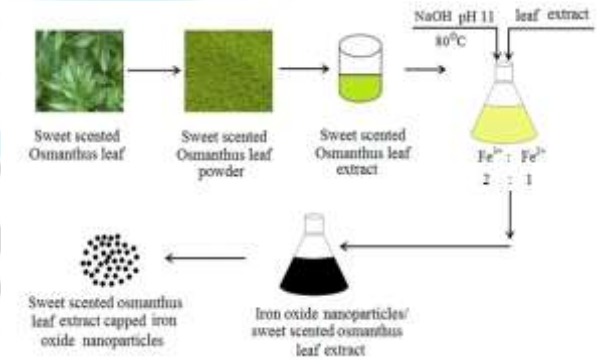

Figure 1: schematic diagram of the synthesis of iron oxide nanoparticles

2.4 Characterization

The reduction of Fe^{3+}/ Fe^{2+} to Fe_3O_4 was confirmed by carrying out UV-Vis study of the synthesized nano particles by the use of UV-2550 Uv-Vis Spectrophotometer Shimadzu Japan in the range of 300 to 800nm. The morphology was studied by employing the use of Scanning electron microscope (SEM) so as to analyze the morphology of the formed iron oxide nano particles via JEOL JSM-6510LV at an accelerating voltage of 20kV. Bruker Tensor 27 Germany with OPUS software was engaged in the evaluation of the FTIR analysis of the IONPs in the range of 400-4000cm^{-1} by using potassium bromide (KBr) in order to study the functional groups present in the synthesized NPs. The thermal

stability of the prepared synthesized IONPs was studied by using SDT Q 600 TGA (T.A. Instruments-water LLC, Newcastle, DE, USA) from room temperature to 1000^0C at a heating rate of 20^0C/min under nitrogen atmosphere. The XRD patterns of the iron oxide nano particles were examined by using X`Pert PRO X-ray diffractometer so as to study the crystslinity of the synthesized AgNPs at 40 kV and 40mA at room temperature in the range from 2 theta = 20^o to 85^o. Zetasizer Nano 3600 was employed in the evaluation of the size of our IONPs.

3. Results and Discussions

3.1 Optical Study

Uv-Vis analysis curve in figure 2 shows the optical absorbance of our IONPs. Colloidal Fe_3O_4 was used as the sample while deionized water was utilized as the reference. The test was done by using two quartz cells in which one of the cells contained deionized water as the reference while the other contained the synthesized nano particles. The absorbance spectrum of the IONPs in figure 2B shows continuous adsorption in the visible range of 300nm to 800nm without any strong adsorption peak. Similar curve has been observed by some other researchers [33, 36]

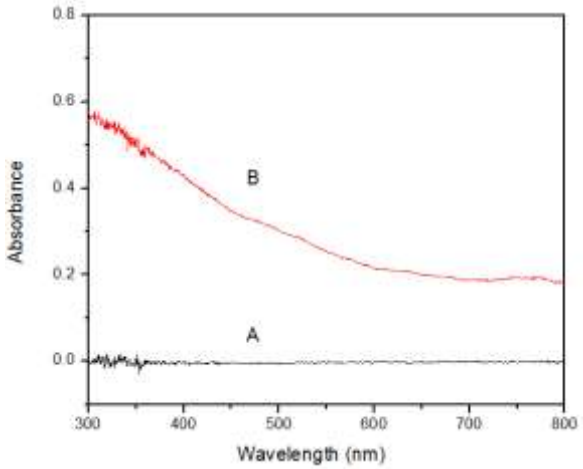

Figure 2: Uv-Vis curve of (A) sweet scented osmanthus leaf extract and (B) synthesized IONPs

3.2 Morhological Analysis

Scanning Electron Microscope (SEM) was used to study the morphology of the synthesized nano particles. The nano particles were coated on a fabric material and the iron oxide nano particles coated fabric was allowed to dry then it was carbon coated and examined using SEM at an accelerating voltage of 20kV. The SEM image in figure 3 shows that the IONPs are spherical in shape and have a uniform spherical shape.

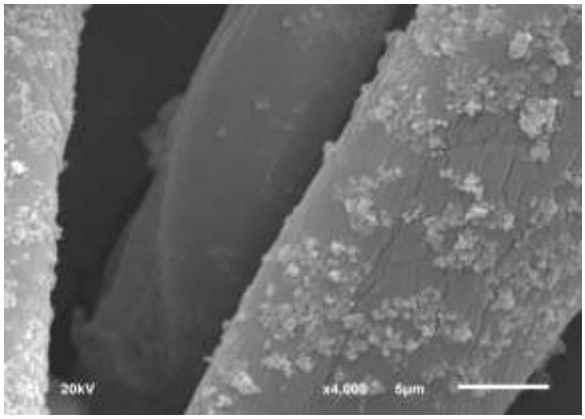

Figure 3: SEM image of the synthesized IONPs.

3.3 Chemical Characterization of the IONPS

FTIR study was carried out in other to evaluate the functional groups of the leaf extract and the iron oxide nano particles. As seen in figure 4A, the FTIR spectra of the leaf extract shows the presence of various functional groups. The peak 3414cm^{-1} indicates OH stretch, the peaks at 2924cm^{-1} and 2855cm^{-1} show methylene C-H asymmetric and symmetric stretch respectively, the peak at 1729cm^{-1} is indicative of the presence of ketone or carboxylic acid, 1650cm^{-1} showing alkenyl C=C stretch, 1514cm^{-1} is for C=C-C aromatic ring stretch, 1456cm^{-1} relates to methylene C-H bend, 1270cm^{-1} and 1320cm^{-1} are indicating OH in plane, 1040cm^{-1} and 1155cm^{-1} are showing skeletal C-C vibrations, 775cm^{-1} and 825cm^{-1} are evidence of aromatic C-H out of plane bend, 667cm^{-1} signifies alkyne C-H bend and 603cm^{-1} represents S-S stretch. These functional groups are responsible for the reduction of the iron salt to Fe_3O_4 as shown in figure 4B, which shows the functional groups responsible for the reduction to IONPs. The peak at 3390cm^{-1} denotes OH stretch, 2925cm^{-1} connotes methylene C-H asymmetric stretch, 1710cm^{-1} implies ketone or carboxylic acid, 1632 shows alkenyl C=C stretch, 1523cm^{-1} relates to C=C-C aromatic ring stretch, 1384cm^{-1} is an evidence of C-H gropup, the peak at 1275cm^{-1} means OH in plane bend, 1073cm^{-1} and 1040cm^{-1} are showing skeletal C-C vibrations, 672cm^{-1} relates to alkyne C-H bend while the peaks from 410cm^{-1} to 535cm^{-1} are indicating Fe-O bonds of Fe_3O_4.

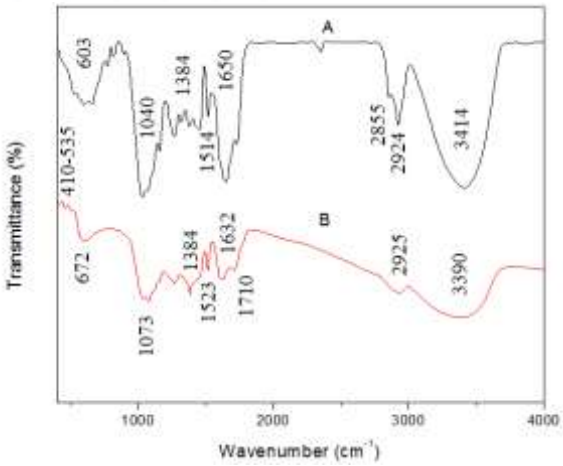

Figure 4: FTIR curve of (A) sweet scented osmanthus leaf extract and (B) synthesized IONPs

3.4 Thermal Analysis

The TG curve of the synthesized IONPs is shown in figure 5. It was carried out from room temperature to 1000°C in an inert nitrogen atmosphere. The curve exhibited continuous weight loss as the temperature increased from room temperature to 1000°C as the curve showed four different stages of weight loss, the first stage was from 51.43°C to 200°C, the second stage from 200°C to 500°C, the third stage from 500°C to 828°C and the last stage from 828°C to 1000°C.

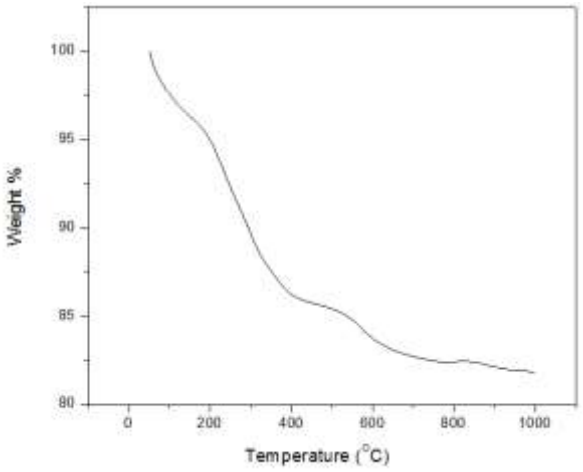

Figure 5: TG curve of the IONPs

3.5 Structural Characterization

The composition of our IONPs was characterized by X`Pert PRO X-ray diffractometer as illustrated in figure 6. It exhibited peaks at; 30.20°, 35.57°, 43.26°, 53.29°, 57.26°, 62.62°, 68.27° and 74.49° corresponding to 220, 331, 400, 422, 551, 440, 533 and 553 respectively which indicates the inverse spinel structure of our Fe_3O_4.

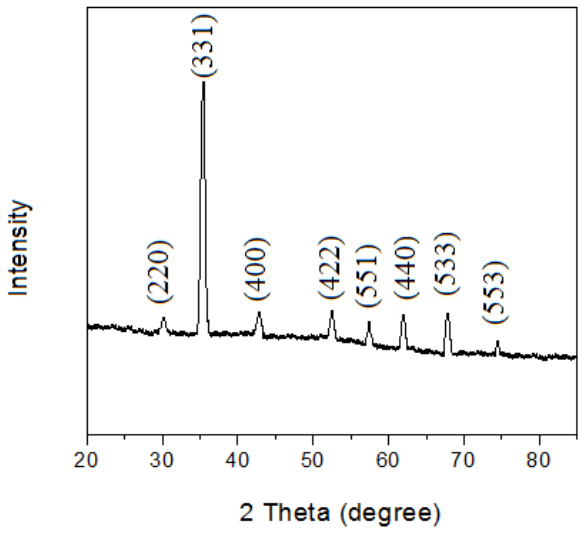

Figure 6: XRD curve of the synthesized nano particles

3.6 Size Distribution

The size of the synthesized IONPs was evaluated by using zetasizer nano 3600 so as to ascertain the size of the nano particles. The size distribution curve is shown in figure 7 and it can be seen that the nano particles are in the size range of 20.25nm to 27.04nm. The average size of of the synthesized nano particles is 23.44nm.

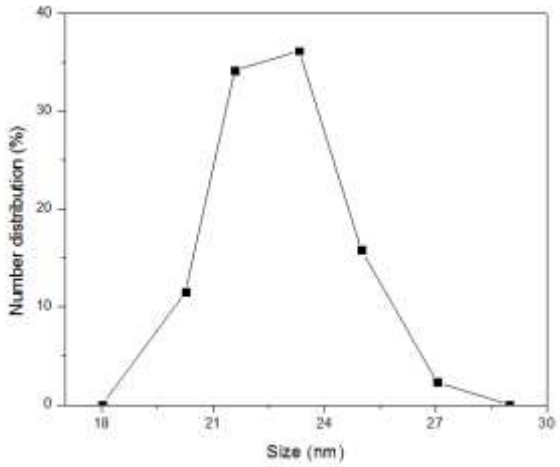

Figure 7: size distribution curve of the synthesized iron oxide nano particles

4. Conclusion

Iron oxide nano particles (Fe_3O_4) were successfully synthesized using our novel method which is an ecofriendly technique whereby, sweet scented osmanthus frangrance leaf extract was used to synthesize the IONPs. The leaf extract acted as a reducing and capping agent. The surface morphology of the nano particles shows that they are spherical in shape. The formation of Fe_3O_4 was confirmed by the FTIR peaks from 410cm^{-1} to 535cm^{-1}. The synthesized nano particles have potential application in antimicrobial activities, magnetic imaging, cancer treatment, sensor waste water treatment, biomedical field, magnetic storage devices, etc.

Declaration of Interest

The authors declare that, “there is no conflict of interest regarding the publication of this paper”.

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