RESEARCH PAPER

Eco-Friendly Synthesis and Characterization of Iron Nanoparticles Using Crude Extract from Eucalyptus Globulus Leaves as Reducing and Capping Agents

***Mahadi Danjuma Sani*[1,2]*, Abdullahi Adamu*[3,*]*, Satish Kumar Ameta*[4]*, Nura Umar Kura*[1]**

[1] *Department of Environmental Science, Federal University Dutse, (Jigawa) Nigeria.*

[2] *Department of Environmental Science, GITAM Deemed University, Visakhapatnam, India.*

[3] *Department of Physics, Faculty of Science and Technology, Mewar University Chittorgarh (Raj.) India.*

[4] *Department of Environmental Science, Mewar University, Gangrar, Chittorgarh (Rajasthan) India.*

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ABSTRACT

In this work, Eucalyptus leaf extract was used as a reducing and capping agent to synthesize Iron nanoparticles (Fe-NPs) using iron (III) chloride as a metal iron salt. The synthesized nanoparticles were later characterized using various techniques. UV-Visible spectroscopy results show that Fe^{3+} was successfully reduced to Fe^{o}/Fe-NP with high absorption at a range of 217-300nm. In addition, FESEM/EDS results indicate that the particles possess irregular shapes together with a few spherical and cubic shapes of various sizes with an average diameter of about 70nm. Further, the EDS result confirms the chemical composition and stoichiometry of the particles. For example, iron was found to be in higher quantity together with oxygen, carbon and chloride. The FTIR results indicate most prominent peaks of functional groups belonging to important phytochemicals which serve as reducing and capping agents. The peaks were 3224.74, 1744, 1055 and 539.99 cm^{-1} which correspond to O-H group of phenolic acids and polyphenols, C=O stretching vibration in aldehydes and ketones, C-O-C of carboxylic acids and FeO/Fe-NPs stretching, respectively. The successful formation of Fe-NPs using the leaf extract of Eucalyptus is a great indicator that toxic chemicals can be eliminated from the conventional methods of synthesizing nanoparticles.

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INTRODUCTION

Nanotechnology has been defined in various ways by various scientists based on different factors and parameters. Khare, et al., 2014 [1] defined nanotechnology as a new and evolving branch of science which involves the engineering of nano-size or smaller particles of different materials through various processes. In addition, it can be described as a science that uses or produces minute particles of nano size which have applications in different fields including industrial activities in electronic equipment, pesticides, and pharmaceuticals, to name a few. Pharmaceutical nanotechnology, according to Bhatia (2016), is the most recent development in pharmaceuticals which provides a variety of opportunities in drug formation and other uses. These days, this emerging technology or science has various applications throughout the globe.

Conventional methods of synthesizing nanoparticles, mainly physical and chemical ones, are typically expensive and pose a threat to environment [3] and public health since they require

* Corresponding Author Email: *adamu.abdullahi012@gmail.com*

a lot of toxic substances and energy. However, green methods involved in the synthesis of nanoparticles have provided a new environmentally friendly technique which poses less of a risk to public health, ecosystem, and environment. Green nanotechnology implements green techniques in the synthesis of nanoparticles that can be applied in various fields. As a multidisciplinary field, green nanotechnology is a rapidly emerging research area which emphasizes making clean, non-hazardous, and particularly environmentally friendly procedures [4]. The synthesis of nanoparticles using plant extract is one of the ever-evolving green technologies or nanotechnologies which employs certain phytochemicals from plant extract to reduce various substances, notably heavy metals, for diverse applications. These green synthesized nanoparticles from heavy metals have a wide range of uses in a variety of fields including agriculture (pesticides)[5], pharmaceuticals (drug formation) [2], environmental water treatment, and removal of heavy metals from the environment (remediation) [6] and many others.

Applying these new and emerging green technologies will drastically reduce the amount of toxic substances in the environment and their effects on public health. However, it has not yet been conclusively demonstrated that such synthesized nanoparticles have no negative impact on the environment and public health. Nonetheless, if they are synthesized through more eco-friendly methods which use biota, they pose less of a threat to the environment. Saratale et al., 2018 [3] reported that the biological methods of synthesizing nanoparticles include microbial methods (using bacteria, actinomycetes, fungi, yeast, and viruses), plant (using different plant parts that include leaves, flower, seed, root, and bark) base methods, algae (using microalgae and macroalgae), and biomimetic (using DNA, protein, enzymes, viruses, pollen, cells and waste biomass).

Green synthesis of Fe

This work aimed at the plant-based synthesis of Fe-NPs using Eucalyptus leaf extract. The method is eco-friendly, requires less amount of energy, and is without toxic chemicals.

MATERIALS AND METHODS

Sample Collection

The plant material (*Eucalyptus globulus* leaves) was obtained from the vicinity of Mewar University. The leaves were collected from the middle age eucalyptus trees, identified and authenticated by the Botany Section of the Life Science Department of the university.

Sample Preparation

The leaves (*E. globulus* leaves) were properly washed with distilled water and dried with air at room temperature in the laboratory for 2 weeks. Afterwards, the dried leaves were ground using mortar and pestle, and the obtained powder was collected in a container [7,8].

Extraction

10g of the ground powder obtained from the plant leaves was weighed and mixed with 200ml of distilled water in a beaker. The solution was then placed on a heating mantle for 15 minutes at 65^0 degrees. It was allowed to cool and then filtered using Whatman filter paper into a clean measuring cylinder (Johnson & Uwa, 2019 and KSV, 2017).

Synthesis of the Iron Nanoparticle

8.11g of metal $FeCl_3$ (iron(III) chloride) was dissolved in 500ml of distilled water in a round bottom glass container to obtain 0.1M of the desired $FeCl_3$ which was brownish in color [9-11].

The synthesis of the nanoparticle followed the modified procedure of [10]. A solution of 1:4 plant extract and iron(III) chloride solution was carefully prepared in 5 different containers. Each of these containers contain 40ml of 0.1M of iron(III) chloride solution and 10ml of the plant extract solution. The color of the iron(III) chloride solution immediately changed from yellowish brown to black after adding the plant extract into the solution which indicates the reduction of the $FeCl_3$ and formation of Fe-NPs. The solutions were then kept in dark and wrapped with foil paper to avoid further chemical reactions for 2 days to complete the formation of Fe-NPs.

Purification And Centrifugation

After completion of the reaction, dry powder of Fe-NPs was obtained by centrifuging at 3500rpm for 5 minutes and the colloidal solution containing Fe-NP was obtained according to [11]. This process of centrifugation was repeated three times to better separate Fe-NPs. Absolute ethanol was used to remove the remaining aqueous liquid associated with the Fe-NP and air-dried at room temperature on a Petri dish.

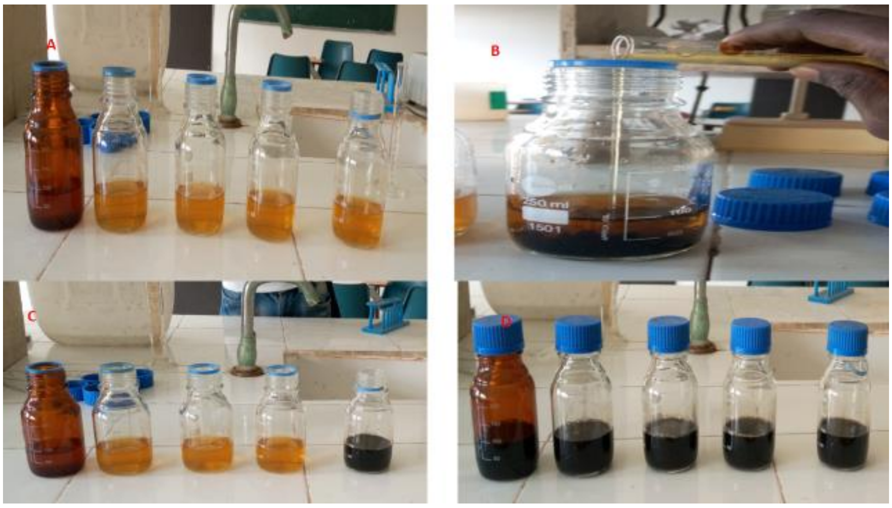

Fig. 1. Depiction of the whole synthesis process.

Characterization Of Fe-Nps

Iron nanoparticles, synthesized using iron(III) chloride metal ions and eucalyptus leaf extract as reducing agents, were characterized by FESEM/ EDS analysis, UV-Visible spectrophotometer, and FTIR analysis.

Field Emission-Scanning Electron Microscopy (FE-SEM)/ Energy Dispersive X-Ray Analysis (EDX) or Energy Dispersive Spectroscopy Analysis (EDS).

FE-SEM technique was employed to visualize the surface morphology (size and shape) of the synthesized Fe-NPs. The morphology of the air-dried synthesized Fe-NPs was examined using Nova Nano FE-SEM 450 (FEI) (dwell 10μs) armed with EDS, which provides ultrahigh resolution characterization and analysis giving precise, true nanometer scale information of the synthesized Fe-NPs. The structural composite of the iron nanoparticles was recorded using Energy Dispersive X-ray spectroscopy (EDS, Sigma). The energy of the electron beam was kept at 15 keV for both imaging and EDX analysis.

Ultraviolet-Visible (UV-Vis) Spectroscopy

Iron nanoparticles were characterized by using a UV–Visible spectrophotometer which is a valuable tool for the structural characterization of metal nanoparticles. The measurement of the absorption spectra was recorded with LAMBDA 750 (Perkin Elmer) UV-Vis NIR Spectrophotometer operated at a resolution of (4 nm). The sample pattern was recorded at 200 to 800 nm wavelength.

Attenuated Total Reflection-Fourier Transform Infrared Spectroscopy (ATR-FTIR) Analysis

FTIR analysis was performed to determine the functional groups causing the eucalyptus leaf extract mediated biosynthesized Fe-NPs using FT-IR Spectrum 2 (Perkin Elmer) in an ATR-FTIR mode. The FTIR spectrum was recorded in the range of 4000 to 400cm^{-1} at a resolution of 4 cm^{-1}. Sample preparation was performed by mixing 10mg (a small amount) of the dried silver nanoparticle in KBr pellets.

RESULTS AND DISCUSSION

Sample preparation

According to Fig. 1, (1A) represents the partition of the iron (III) chloride solution which was used to synthesize Fe-NPs, whereas (1B) shows the applications of *E. globulus* extract for the iron (III) chloride solution which turns black immediately indicating the formation of iron nanoparticles.

Fig. 2. Powdered form of Fe-NP after drying.

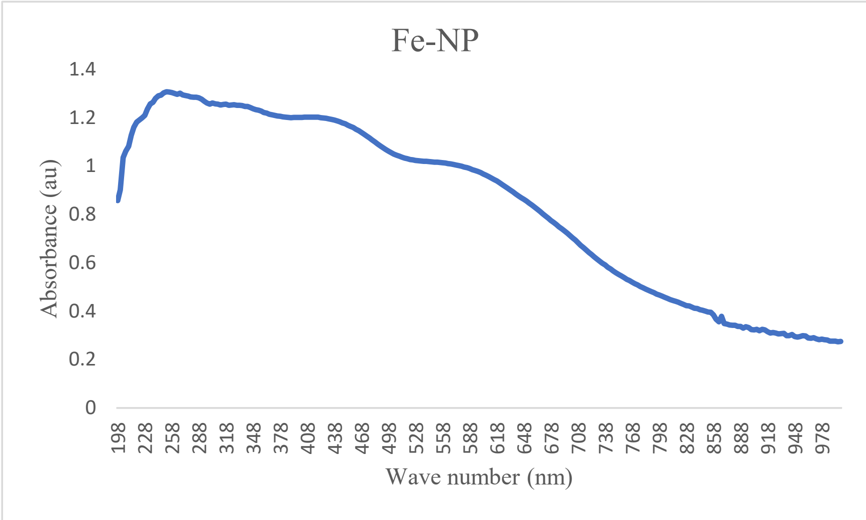

Fig. 3. UV-Visible spectrum of Fe-NPs.

However, (1C) and (1D) depict the outcome of the synthesized Fe-NPs which were settled later on by means of gravity in a centrifuging machine.

Characterizations

UV-Vis Analysis of Fe-Nps

As a valuable tool for the characterization of metallic nanoparticles, UV-Visible spectroscopy was employed to characterize the sample to ascertain the formation of Fe-NP. In this work, the formation or reduction of Fe^{3+} into zero-valent iron nanoparticles with peaks at a range equal to that of Fe-NPs is inferred by using UV-Visible spectroscopy. Based on Fig. 3, it is observed that the UV spectrum of the synthesized metallic iron nanoparticle which peaks at a range between 217-300nm is identical to the UV spectral of the metallic iron nanoparticle [12]. It can be inferred that Fe-NP may have been formed successfully. This result is in line with the spectral bands reported by [8,10,13]. In addition, the reported absorption peaks at a range between 210 and 240 were similar to the characteristics of UV spectra of metallic iron. However, in other studies, the spectral bands differ which may be due to impurities that can be avoided by proper handling of the particles, the nature of

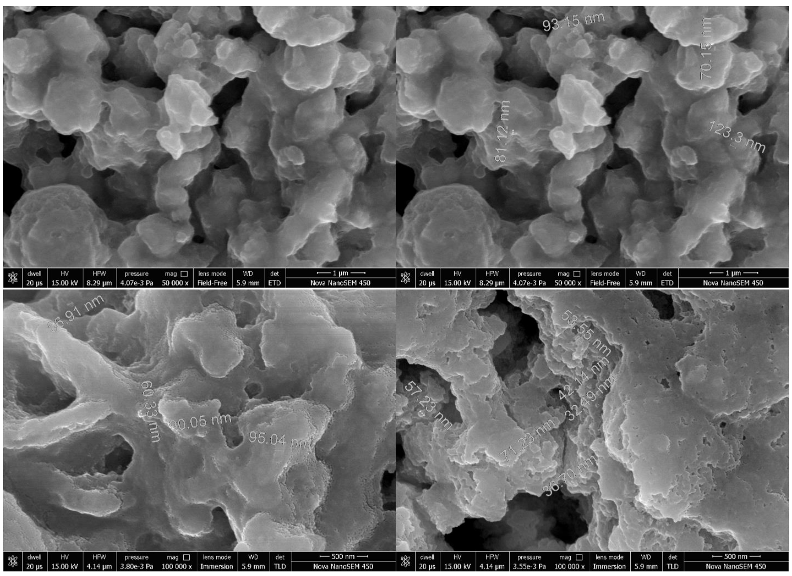

Fig. 4. FESEM images showing the morphology and size of Fe-NPs.

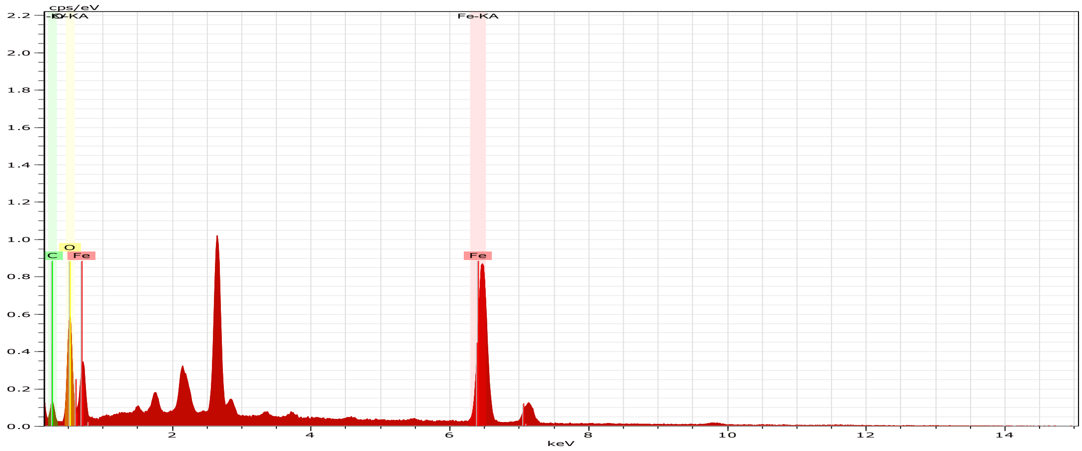

Fig. 5. EDS Chart of Fe-NPs.

plant extract, and phytochemicals present, or the concentration of the metallic salts employed. [14] observed a peak at 371.71 nm which was inferred to belong to iron oxide nanoparticles. [15] reported a peak at a region between 400-450 nm, and [16] obtained peaks at a range of 300-500 nm. Phenolic compounds are the major precursors in the capping and/or stabilization of Fe-NPs [10].

FESEM And EDS Analysis of Fe-Nps

FESEM was used to determine the surface morphology, structure, and size of the synthesized nanoparticles. The images obtained and the corresponding EDS chart and mapping imageries are shown below with various information regarding the Fe-NPs.

According to Fig. 4, it is observed that the nanoparticles come in various shapes, most of which are irregular with few spherical and granular shapes in nature [8]. The particles are capped by the capping agents in the leaf extract of the plant which is indicated by the cover on the particles. In addition, there exists an agglomeration at various points which may be attributed to the presence of bioactive compounds on the surface of the particles [17].

The particle size/diameter is in the range of 32nm-129nm with an average diameter of about 70nm. This result is almost similar to that of [16] with 99-129nm, [10] within the range of 200nm and [18] 15-100 nm.

EDS analysis was conducted to further determine the elemental composition and stoichiometry of the iron nanoparticles. The result indicates signals that iron is present together with other elements at various levels. According to Fig. 5 and Table 1, it can be seen that, apart from iron, oxygen and carbon are also present in a significant amount which may likely be from the plant extract. Other elements may also be present in a minute quantity that may include chlorine from the metal salt used (iron (III) chloride), silicon, and aluminum from the glass wares and other apparatus used.

FTIR Study of Fe-Nps

FTIR is an important tool for characterizing nanoparticles and determining the major functional groups present in the plant extract (phytochemicals) that plays a role in the formation of Fe-NPs and other metallic nanoparticles. FTIR spectra analysis was conducted to determine the active biomolecules responsible for the reduction and stabilization of Fe-NPs at a wave-number range of 400-4000 cm^{-1} (Fig. 6).

Table 1. Elemental composition of the sample by EDS.

Element	A.N.	Series	Unn. C (wt %)	Norm. C (wt %)	Atom. C (at %)	Error	(1 Sigma) (wt %)
Fe	26	K	46.51	80.77	51.85		1.40
O	8	K	7.15	12.41	27.81		0.99
C	6	K	3.92	6.82	20.34		0.72
		Total	57.59	100.00	100.00		

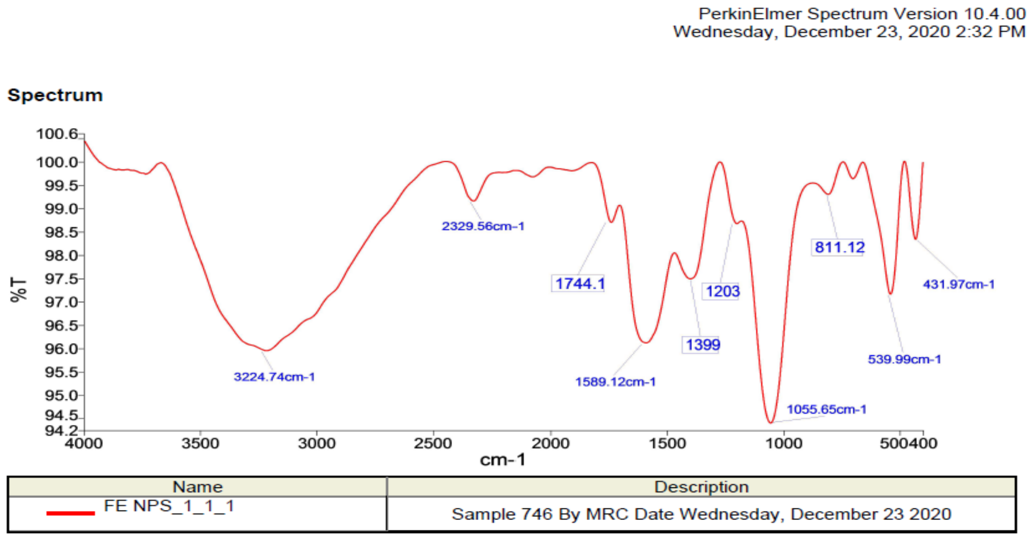

Fig. 6. FTIR spectrum of Fe-NPs.

The existence of the most prominent and strong peaks of various wave numbers representing functional groups belonging to phenolic compounds, carboxylic group, aromatic alkenes, aldehydes, and other groups which act as reducing, capping agents and antioxidant activity suggest the successful formation of Fe-NPs. The strong and broad peak at 3224.74 cm^{-1} wave number corresponds to the O-H stretching vibration of polyphenols and phenolic acid. This value is in agreement with that of [17] at a range of 3500–3200 cm^{-1} indicating the vibrational stretching of O-H polyphenolic group. [19] represents the polyphenolic compound which serves as a reducing agent at a similar range of 3500-3200 cm^{-1}. [7] at 3270 cm^{-1} and [16] at 3200 cm^{-1} stand for phenolic compounds. Other findings include [9] at 3419 cm^{-1}, [20] in a range between 3400 and 3430 cm^{-1} suggesting the presence of phenolic compounds which can reduce Fe^{2+} to Fe^0. Additionally, [10] at 3420 cm^{-1} corresponds to O-H bond stretching in the phenolic group. The phenolic (O-H) group is one of the major precursors in plants that plays a significant role in the reduction and stabilization of metallic Fe^{3+} into zero-valent Fe-NP [7,10,13,18,21–23].

Moreover, the FTIR bands at 1589.12 cm^{-1} correspond to the C=C bonds of aromatic compounds or unsaturated alkenes [24]; 1055 cm^{-1} represents C-O-C (CHO) bonds of carboxylic acids which mostly serve as a capping agent [11], and 539.99 cm^{-1} corresponds to Fe-NPs band of FeO which confirms the successful synthesis of iron nanoparticles [15–17,22, 24, 25]. The peaks at 2329 cm^{-1}, 1744 cm^{-1}, 1399 cm^{-1} and 1203 cm^{-1} may be attributed to C-H stretching, C=O stretching in aldehydes and ketones (indicating the presence of phenolic acid and terpenoids), C-N in aromatic amines, and symmetrical wagging of C-H, respectively [13].

The appearance of the aforementioned peaks in the FTIR spectra of *E. globulus* extract and Fe-NPs at various wave numbers indicates the activity of certain phytochemicals in the extract that serve as reducing and capping agents in the biosynthesis of Fe-NP or zero-valent Fe. These phytochemicals include phenolic acids, polyphenols, terpenoids, and flavonoids [26].

CONCLUSIONS

The successful formation or synthesis of Fe-NPs using the leaf extract of Eucalyptus is a great indication that toxic chemicals can be eliminated from the conventional methods of synthesizing nanoparticles. Fe-NPs have been reported in the literature to possess high efficacy towards remediation of the environment and other sectors, which include, but are not limited to, pharmaceutical industries, microbial activity, medical sectors, and many other fields. However, toxic and harmful substances that are highly detrimental to health and other aspects of the environment may be discharged into the environment when substances are synthesized using the procedures of conventional method. The green methods of synthesizing metallic nanoparticles provide an avenue for industries and other sectors to avoid using harmful chemicals or huge amounts of energy in the field of nanoparticle synthesis.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

REFERENCES

[1] S. Khare KW, and K. Gokulan. Nanotechnology. Encycl Food Microbiol Second Ed2014. p. 893-900. https://doi.org/10.1016/B978-0-12-384730-0.00406-7

[2] Bhatia S. Natural polymer drug delivery systems: Nanoparticles, plants, and algae: Springer; 2016. https://doi.org/10.1007/978-3-319-41129-3

[3] Sorbiun M, Shayegan Mehr E, Ramazani A, Mashhadi Malekzadeh A. Biosynthesis of metallic nanoparticles using plant extracts and evaluation of their antibacterial properties. Nanochemistry Research. 2018;3(1):1-16.

[4] Saratale RG, Saratale GD, Shin HS, Jacob JM, Pugazhendhi A, Bhaisare M, et al. New insights on the green synthesis of metallic nanoparticles using plant and waste biomaterials: current knowledge, their agricultural and environmental applications. Environmental Science and Pollution Research. 2018;25(11):10164-83. https://doi.org/10.1007/s11356-017-9912-6

[5] Sankar MV, Abideen S. Pesticidal effect of green synthesized silver and lead nanoparticles using Avicennia marina against grain storage pest Sitophilus oryzae. Int J Nanomater Biostruct. 2015;5(3):32-9.

[6] A. A. Ansari SSG, R. Gill, G. R. Lanza, L. Newman. "Phytoremediation: Management of environmental contaminants," Phytoremediation Manag. Environ. Contam.2019. 1-476 p. https://doi.org/10.1007/978-3-319-99651-6

[7] Katata-Seru L, Moremedi T, Aremu OS, Bahadur I. Green synthesis of iron nanoparticles using Moringa oleifera extracts and their applications: Removal of nitrate from water and antibacterial activity against Escherichia coli. Journal of Molecular Liquids. 2018;256:296-304. https://doi.org/10.1016/j.molliq.2017.11.093

[8] Johnson A, Uwa P. Eco-friendly synthesis of iron nanoparticles using Uvaria chamae: Characterization and biological activity. Inorganic and Nano-Metal Chemistry. 2019;49(12):431-42. https://doi.org/10.1080/24701556.2019.1661448

[9] Gottimukkala K, Harika R, Zamare D. Green synthesis of iron nanoparticles using green tea leaves extract. J Nanomed Biother Discov. 2017;7:151.

[10] Da'na E, Taha A, Afkar E. Green Synthesis of Iron Nanoparticles by Acacia nilotica Pods Extract and Its Catalytic, Adsorption, and Antibacterial Activities. Applied Sciences [Internet]. 2018; 8(10). https://doi.org/10.3390/app8101922

[11] Soliemanzadeh A, Fekri M, Bakhtiary S, Mehrizi MH. Biosynthesis of iron nanoparticles and their application in removing phosphorus from aqueous solutions. Chemistry and Ecology. 2016;32(3):286-300. https://doi.org/10.1080/02757540.2016.1139091

[12] Dhuper S, Panda D, Nayak P. Green synthesis and characterization of zero valent iron nanoparticles from the leaf extract of Mangifera indica. Nano Trends: J Nanotech App. 2012;13(2):16-22.

[13] A. Bouafia and S. E. Laouini. Green synthesis of iron oxide nanoparticles by aqueous leaves extract of Mentha Pulegium L.: Effect of ferric chloride concentration on the type of product Materials Letters. 2020;265:127364. https://doi.org/10.1016/j.matlet.2020.127364

[14] al. IBe. Green synthesis of iron oxide nanoparticles using pomegranate seeds extract and photocatalytic activity evaluation for the degradation of textile dye Journal of Materials Research and Technology. 2019;8(6):6115-24. https://doi.org/10.1016/j.jmrt.2019.10.006

[15] Turakhia B, Turakhia P, Shah S. Green synthesis of zero valent iron nanoparticles from Spinacia oleracea (spinach) and its application in waste water treatment. J Adv Res Appl Sci. 2018;5(1):46-51.

[16] Devatha CP, Thalla AK, Katte SY. Green synthesis of iron nanoparticles using different leaf extracts for treatment of domestic waste water. Journal of Cleaner Production. 2016;139:1425-35. https://doi.org/10.1016/j.jclepro.2016.09.019

[17] Abdullah JAA, Salah Eddine L, Abderrhmane B, Alonso-González M, Guerrero A, Romero A. Green synthesis and characterization of iron oxide nanoparticles by pheonix dactylifera leaf extract and evaluation of their antioxidant activity. Sustainable Chemistry and Pharmacy. 2020;17:100280. https://doi.org/10.1016/j.scp.2020.100280

[18] Luo F. Green Synthesis of Iron Nanomaterials by Grape Leaf Extract and their Application in Removal of Contaminant. Australia: The University of Newcastle; 2016.

[19] Murgueitio E, Debut A, Landivar J, Cumbal L. Synthesis of iron nanoparticles through extracts of native fruits of Ecuador, as capuli (Prunus serotina) and mortiño (Vaccinium floribundum). Biology and Medicine. 2016;8(3):1. https://doi.org/10.4172/0974-8369.1000282

[20] Fazlzadeh M, Rahmani K, Zarei A, Abdoallahzadeh H, Nasiri F, Khosravi R. A novel green synthesis of zero valent iron nanoparticles (NZVI) using three plant extracts and their efficient application for removal of Cr(VI) from aqueous solutions. Advanced Powder Technology. 2017;28(1):122-30. https://doi.org/10.1016/j.apt.2016.09.003

[21] Rong K, Wang J, Zhang Z, Zhang J. Green synthesis of iron nanoparticles using Korla fragrant pear peel extracts for the removal of aqueous Cr(VI). Ecological Engineering. 2020;149:105793. https://doi.org/10.1016/j.ecoleng.2020.105793

[22] Murgueitio E, Cumbal L, Abril M, Izquierdo A, Debut A, Tinoco O. Green Synthesis of Iron Nanoparticles: Application on the Removal of Petroleum Oil from Contaminated Water and Soils. Journal of Nanotechnology. 2018;2018:4184769. https://doi.org/10.1155/2018/4184769

[23] Pan Z, Lin Y, Sarkar B, Owens G, Chen Z. Green synthesis of iron nanoparticles using red peanut skin extract: Synthesis mechanism, characterization and

effect of conditions on chromium removal. Journal of Colloid and Interface Science. 2020;558:106-14. https://doi.org/10.1016/j.jcis.2019.09.106

[24] Madivoli ES, Kareru PG, Gachanja AN, Mugo SM, Makhanu DS. Phytofabrication of iron nanoparticles and their catalytic activity. SN Applied Sciences. 2019;1(8):879. https://doi.org/10.1007/s42452-019-0951-0

[25] Yan W. Iron-based nanoparticles: Investigating the nanostructure, surface chemistry, and reactions with environmental contaminants: Lehigh University; 2011.

[26] Sadhasivam S, Vinayagam V, Balasubramaniyan M. Recent advancement in biogenic synthesis of iron nanoparticles. Journal of Molecular Structure. 2020;1217:128372. https://doi.org/10.1016/j.molstruc.2020.128372