Journal of **N**onlinear **A**nalysis and **O**ptimization
Vol. 15, Issue. 1, No.3 : 2024
ISSN : **1906-9685**

PHYTOCHEMICAL MEDIATED SYNTHESIS AND CHARACTERIZATION OF IRON NANOPARTICLES

S. KAVITHA Research scholar, Department of Zoology, Thiruvalluvar University, Vellore-5, Tamil Nadu, India Email: gsvelu@gmail.com
P.SUGANYA Department of Zoology, Thiruvalluvar University, Vellore-5, Tamil Nadu, India
S.KARTHIKEYAN School of Bioscience & Technology, Vellore Institute of Technology, Vellore-4.Tamil Nadu, India.
G.SINGARAVELU Department of Zoology, Thiruvalluvar University, Vellore-5, Tamil Nadu, India
K.JAYACHANDRAN[4] Department of Zoology, Annamalai University, PG Extension Centre, Villupuram-1, Tamil Nadu, India

Abstract

Iron is one of the extensively explored transition metals because of its remarkable crystal structures, low cost, magnetic properties, different oxidation states the eco-friendly nature. Present report demonstrates green principle mediated synthesis of iron nanoparticles which was achieved using the medicinally important leaf extract of *Cassia auriculata.* Rapid synthesis of iron nanoparticles was observed further the nanoparticles synthesized are stable for more than one year. Newly synthesized iron nanoparticles was characterized using UV-Vis spectroscopy, FTIR, TEM, SEM with EDX and XRD.

Keywords: Phytochemical synthesis, Iron nanoparticles.

1. Introduction

Nanoscience is a transdisciplinary field of research evolving as a prominent technology that involves the design and engineering of functional systems at the molecular range. Recent days, nanotechnology is an emerging and dynamic research area in current materials science and is growing day by day, it plays an important role in life science. Nanomaterials offer incredible prospects for research and technology advancement in various fields of international priorities. Currently, most of the industrial countries are incorporating nanotechnology in their development systems as they find it as a driving force for wealth creation in the near future (Khan *et al*., 2019; Aakash *et al*., 2020).

Trans-disciplinary nanoscience research involving chemists, physicists, biologists and engineers are concerned about the need for developing environmental friendly and sustainable methods for the synthesis of nanomaterials. There are two basic forms for attaining nanomaterials “top-down” and “bottom-up”. Top-down approach usually involves breaking of big chunks of materials into smaller objects of desired shapes and sizes by either cutting or grinding. Complementary to top-down approach the bottom-up approach involves building up of macrosized complex systems by combining simple atomic level component materials (Yu *et al*., 2013).

Recently, nanoscience has opened a new venue in the development of nanomedicine apart from engineering. Nanomaterials applications have been receiving great potential in recent years. Nanomaterials, particularly owing to their high surface area, exhibit distinctive features that determine the engineering of biological interactions (Singh and Lillard, 2009). Due to the emerging applications of nanomaterials in life science such as drug delivery, diverse range of diagnostic tools etc it is highly imperative to synthesize biocompatible nanomaterials. Conventionally, there are a large number of physical, chemical and hybrid methods available to synthesize different kinds of nanomaterials (Ijas, *et al*., 2020; Della Gaspera, 2021).

Eventhough physical and chemical methods are more popular in the synthesis of nanoparticles, the use of toxic chemicals greatly limit their biomedical applications. In order to address these concerns, developing new synthetic routes based on the reliable, non toxic and eco friendly principles is imperative. Eventually one of the options to achieve this goal is to use biological resources for the synthesis of nanomaterials. Accordingly, present investigation addresses biological synthesis of iron nanoparticles using the green chemistry approach.

Iron nanoparticles have attracted intensive research interest because of their important applications in cancer therapy, drug delivery, magnetic resonance imaging etc (Kudr *et al*., 2017). Furthermore iron oxide nanoparticles have received a great deal of attention because of their biocompatibility and chemical inertness making them suitable for life science application (Siddiqi *et al*., 2016). Present investigation demonstrates biological synthesis of iron nanoparticles using the green chemistry principle of the plant *Cassia auriculata* and their physicochemical characterization.

2.Materials and Methods

Present investigation demonstrates synthesis of iron nanoparticles using the green chemistry approach. Attention was also paid to generate medicinally significant iron nanoparticles for which ethnopharmacological approach has been addressed.

In the pilot experiment a large number of medicinal plants were collected, identified from Vellore District, Tamil Nadu. All the collected plant's different parts, leaves, flowers, root were cut into small pieces, crushed and extracted using distilled water. The extract was prepared into different concentrations and subjected to different concentrations of aqueous ferric chloride. Various experimental conditions were maintained like stirring, change in pH, different temperature in different time intervals. Among different experimental conditions and concentrations, the aqueous leaf extract of *Cassia auricaulata* was found to have the property of synthesizing iron nanoparticles.

2.1. Plant Material

Cassia auriculata profoundly used in Ayurvedic medicine. *C. auriculata* belongs to the family Caesalpiniaceae. The common name is tanners cassia. This shrub in evergreen and has attractive yellow colour flowers that grow in various parts of India as well as other parts of Asia. *C. auriculata* is mainly used traditionally for the treatment of diabetes, rheumatism, conjunctivitis.

Precursor ferric chloride ($FeCl_3$) was purchased from Himedia Laboratories Pvt Ltd., Mumbai. All glasswares have been sterilized in hot air oven prior to use.

2.3.Preparation of *Cassia auriculata* extract

Ten grams of *Cassia auriculata* leaves were washed thoroughly with tap water, followed by de-ionised water. The leaves were ground with mortar and pestle, by using 100ml of de-ionised water. The extract was filtered using whatman No.1 filter paper. Freshly prepared *Cassia auriculata* leaves extract was used for the synthesis of iron nanoparticles (Fig.1).

2.4.Synthesis of iron nanoparticles

From the stock solution, 40ml of fresh leaves extract was taken. Different concentration were examined to identify the particular concentration which reduces the ferric chloride into iron nanoparticle. As a result 40ml of leaf extract was identified as appropriate concentration for the synthesis. Likewise various molar concentration of ferric chloride was prepared among which 0.1M concentration of ferric chloride was found to be optimum for synthesis. The plant extract (40ml) is kept under magnetic stirrer for 40minutes into this 60ml of 0.1M concentration of ferric chloride was added dropwise. The reaction mixture was closely monitored and it was observed that immediate colour change from green to brown was noted. As previously reported the change of colour indicates the reduction of ferric chloride into iron nanoparticles (Fig.1).

3. Results and Discussion

Synthesis of iron oxide nanoparticles using green chemistry approach is intriguing and currently extensive efforts have been invested in this direction. The synthesis of iron nanoparticles was achieved using the aqueous leaf extract of the plant *Cassia auriculata.* The bioreduction of ferric ions in aqueous solution was measure by UV-visible spectroscopy in the range of 200-600 nm and it was confimed that the surface Plasmon vibration occurs at 286nm (Fig.2).

The FT-IR spectroscopy demonstrated the development of nanoparticles, as displayed in figure 3, which shows the FT-IR spectra of the iron NPs. The peaks of strong absorption at 598cm^{-1} were assigned to the band vibrations of Fe-O. The transition at 1084cm^{-1} was confirmed to C-N stretch. The bands at 1440 cm^{-1} were due to C-H bending, aromatic C–C stretching vibrations. The broad absorption peak band at 1624cm^{-1} was attributed to the bending fluctuations and stretching of the N-H bends and water molecules.

In figure 4, the SEM image of iron nanoparticle clearly indicating the final product possess approximately uniform spherical morphology. EDX is an analytical method used to find the chemical compositions of various elements and determines the relative abundance of particular chemical elements on the solid surface. The EDX spectrum determined the presence of iron and oxide. EDX measured the weight percentage of iron (16.35%) and oxygen (18.87%). The synthesized iron nanoparticle had 7.78% of iron, 31.35% of oxygen, 35.01% sodium and 25.85% chlorine (Fig 4b).

Figure 1. Photographs of vials comprising
(a) Ferric chloride solution
(b)* Aqueous leaf extract of *Cassia auriculata
(c)* Iron nanoparticles synthesized using *Cassia auriculata

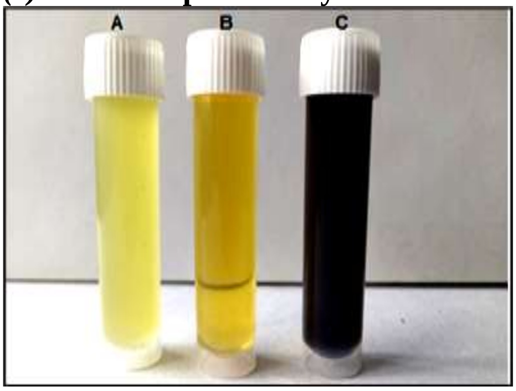


Fig. 2. UV-visible spectral analysis of the newly synthesized iron nanoparticles and the peak was recorded at 286 nm.

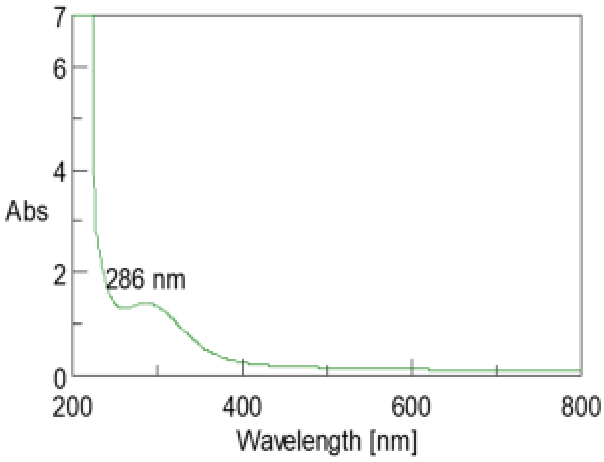
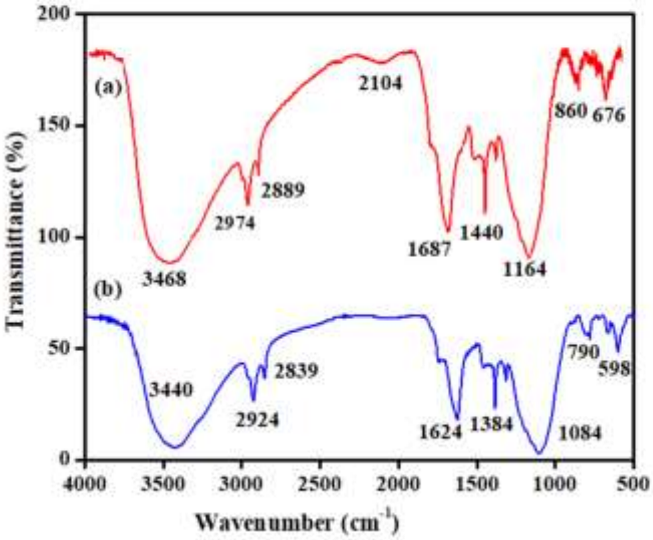


Figure 3. a. FTIR spectrum of aqueous leaf extract of *Cassia auriculata*

FTIR spectrum of Iron nanoparticles` synthesized using the leaf extract of *Cassia auriculata*



Shown in Fig. 5 is a representative TEM micrograph of Fe NPs. As shown in Fig. 5, the particle size distribution of the iron nanoparticles is found to be in the range of 9-14 nm. It reveals that the Fe-NPs are well dispersed and predominantly spherical in shape, while some of the NPs were found to be having structures of irregular shape. The particle size agrees with that calculated from Scherrer equation with average diameter of around 12 nm.

Figure 6 displays the powder XRD pattern of the iron nanoparticles made with the aqueous leaf extract of *Cassia auriculata*. The iron particles' primary strong distinctive peaks may be found at 2θ = 44.5, 65, and 82. These values correlate to the amorphous structure of iron (100), (200), and (211). For iron (PDF-00-006-0696), all of the reflection peaks could be indexed to a rhombohedral structure. These results are comparable to nanoparticles' crystalline structure.

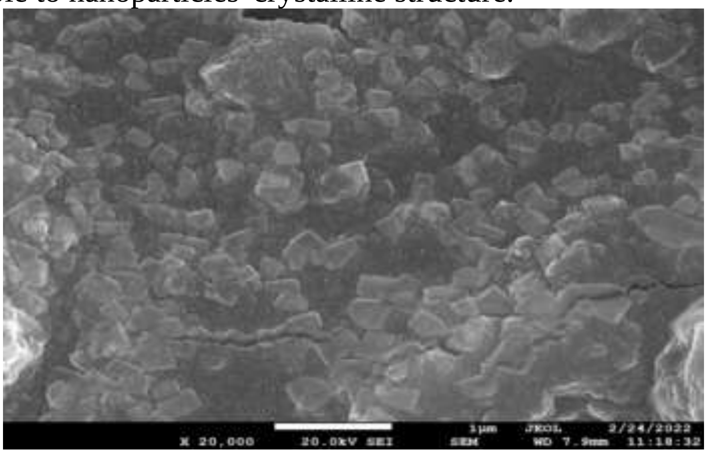


Fig.4.b. EDAX pattern of iron nanoparticles synthesized using *Cassia auriculata* leaf extract

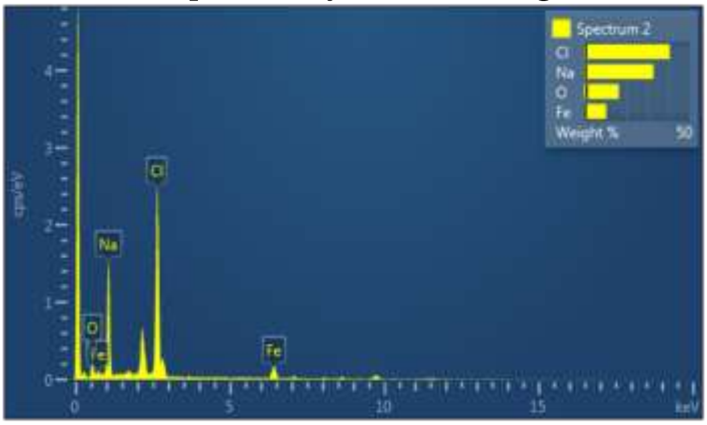


Figure 5. Transmission Electron Micrograph image of iron nanoparticles.

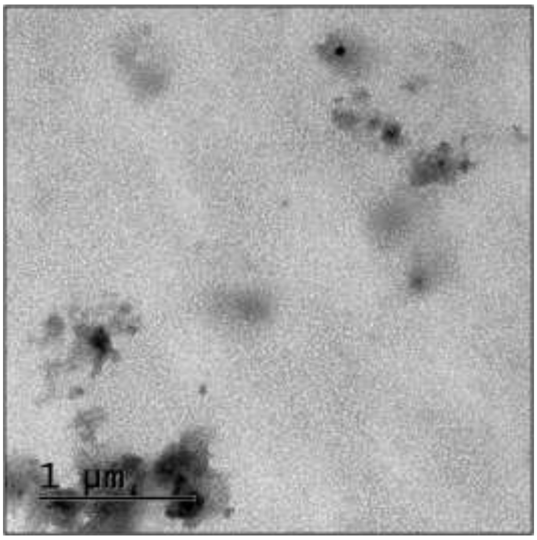
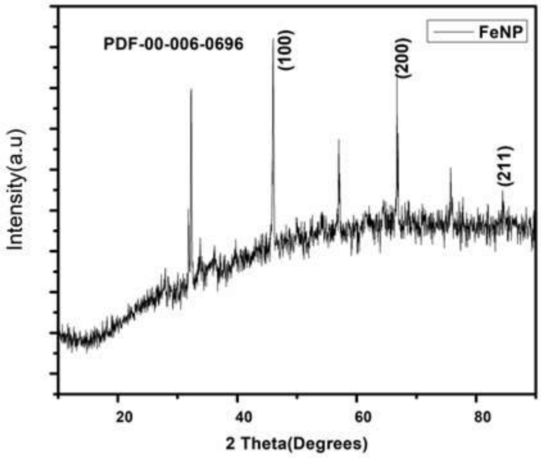


Fig.6. XRD pattern of iron nanoparticles synthesized using *Cassia auriculata* leaf extract



The phenomena of molecular self assembly have inspired interesting development of novel functional nanomaterials for various medical applications. Nanomedicine have emerged as an amazing off-shoot of nanoscience and nanotechnology. Recently nanomaterials have been researched intensively for many high technology applications, including biosensing, drug delivery, gene delivery and pharmaceuticals (Bayda, *et al.*, 2020). It is in this context synthesis biocompatible nanomaterials gains their importance. Green synthesis of nanopaticles has been emerging research area now a day. The advancement of green synthesis over chemical and physical methods is environmental friendly, cost effective and easily scaled up for huge scale synthesis of nanoparticle. Furthermore that there is no need to use high temperature, pressure, energy and toxic chemicals (Brayner *et al*., 2013).

Physical and chemical methods are being used extensively for production of metal and metal oxide nanoparticles. However, this production requires the use of very reactive and toxic reducing agents such as sodium borohydride and hydrazine hydrate, which cause undesired detrimental impacts on the environment, plant and animal life it supports. Researchers continue efforts to develop facile, effective and reliable green chemistry processes for the production of nanomaterials. Various organisms act as clean, eco-friendly and sustainable precursors to produce the stable and well functionalised nanoparticles. These may include bacteria, actinomycetes, fungi, yeast, viruses, etc. (Mandal *et al*., 2006; Jebali *et al*., 2011). Thus, it is vitally important to explore a more reliable and sustainable process for the synthesis of nanomaterials. Economic viability, environmental sustainability, and social adaptability as well as the availability of local resources are a matter of concern in the production of nanomaterials. In order to keep the prices of the final finished nanotechnology-based products affordable to consumers, industries must maintain a delicate balance between environmentally sound green processes and their sustainability. The green nanotechnology-based production processes operate under green conditions without the intervention of toxic chemicals. Based on the facts the results of the present investigation gains their importance.

The green synthesis of iron nanoparticles using various plant extracts has been reported by many researchers. Biosynthesis of iron nanoparticles (Fe NPs) has been mainly performed using extract of green tea which is a cheap and local resource. Hoag and coworkers (2009) synthesised nZVI utilizing green tea (*Camellia sinensis*) extract containing a range of polyphenols. Without the addition of any surfactant or polymer, the stable nanoparticles were obtained at room temperature. Polyphenols in plant act as both a reducing agent and a capping agent, resulting in stable green nanoscale zero-valent iron particles with unique properties. Green tea (20 g/L) was used for preparation of extract. A solution of 0.1 M FeCl3 was added to (20 g/L) green tea extract in a 2:1 volume ratio resulting in spherical nanoparticles with diameter of 5–10 nm. In another study, Shahwan and coworkers (2011) adopted the same procedure for synthesis of iron nanoparticles with little modification. They used the 0.10 M iron chloride solution to green tea in 2:3 volume ratios. Following this, 1.0 M NaOH solution was added until the pH was 6.0 and the formation of nanoparticles was marked by the appearance of intense black precipitate. The iron particles were harvested by evaporating water from the solution. The obtained nanoparticles (40–60 nm) were then employed as a catalyst for the degradation of methylene blue and methyl orange dyes. Moreover, Markova and coworkers (2014) prepared the iron(II, III)-polyphenol complex nanoparticles with a diameter of 70 nm-sized by adding $Fe(NO_3)_3 \cdot 9H_2O$ to the green tea extract. Fe-based nanoparticles were prepared by introducing 0.5 M $Fe(NO_3)_3 \cdot 9H_2O$ into green tea extract in a 1:5 volume ratio under nitrogen atmosphere. Researcher's produced zero valent iron and iron(II, III) polyphenol complex nanoparticles by utilizing green tea extract in different studies. Hence, production of nano iron with different size and properties are due to change in synthesis procedure, and most important ratio of extract to salt. Similar findings were found in study of Nadagouda and coworkers (2010), they evaluated the effect of extract concentration on size of iron nanoparticles. Nanoscale zero valent iron (nZVI) synthesis was done at room temperature using different volumes of tea extract and $Fe(NO_3)_3$ solution. It was found that size and morphology of particles could be change by changing the concentration of extract as well as iron salt.

Actual mechanism of nanoparticles synthesis by living organisms is not yet clear, however studies shows that enzymes produced from bacteria and fungi and biomolecules especially phenolic compounds in plant products cause the production of metallic iron nanoparticle (Bharde *et al*., 2010; Moon *et al*., 2010; Luo *et al*., 2014). In one study, Becerra and coworkers (2010), utilised tannin powder a green reagent for synthesis of iron oxide NPs. Tannins consist of non-toxic polyphenolic compounds which act as reducing and stabilizing agents for the production of iron oxide NPs. According to them, most likely the presence of phenolic-OH groups and ortho-dihydroxyphenyl groups in chemical structure of tannins are involved in the formation of complexes with iron and also take part in redox reactions. In the formation of iron oxide NPs by tannins, the reactions undergo changes in electron structure. Tannins are oxidised to quinines and, by this reaction, iron salt is reduced to iron oxide nanoparticles.

Likewise, presence of biomolecules or combinations of chemically complex biomolecules, e.g., enzymes, amino acids, proteins, Vitamins, and polysaccharides, and organic acids such as citrates, may act as reducing and capping agents in nanoparticle synthesis (Iravani, 2011).

In the green chemistry approach not a single biomolecule of plant extract was involved in the fabrication of nanoparticles. Various plant components are rich in secondary metabolites and responsible for synthesis of metallic nanoparticles. Secondary metabolites include the polyphenols, flavonoids, tannic acid, terpenoids, ascorbic acids, carboxylic acids, aldehydes and amides. Many reducing sugars are commonly found in plants, and their presence is confirmed by the IR spectroscopic technique in different studies (Huang *et al*., 2013). Phyto-chemicals in plant extracts possess ideal redox properties that allow efficient reduction of metal precursors for conversion into their corresponding metallic nanoparticles.

Many approaches have been reported for iron nanoparticles synthesis such as ball milling, sol-gel, high-energy electro-deposition (Maliar *et al*., 2012), coprecipitation laser–induced gas phase pyrolysis, chemical vapor condensation, and freeze-drying (Rashmi *et al*., 2013). Chemically, the formation of iron nanoparticles can be attained through the reduction of iron organic or inorganic salt or via reduction of an iron oxide. Iron nanoparticles have been synthesized by sodium borohydride or lithium triethylborohydride as a reducing agent (Rashmi *et al*., 2013).

Green synthesis of iron nanoparticles has attracted much attention from researchers as it decreases nanoparticles aggregation and thus improves stability. In addition, it is an environmentally friendly method of eliminating the use of sodium borohydride as a reducing agent, which is very corrosive and flammable (Shahwan *et al*., 2011). Furthermore, using plant extracts as reducing agent offer suitability for biomedical and pharmaceutical applications since no toxic chemicals are used during synthesis (Kanagasubbulakshmi and Kadirvelu, 2017). Green Iron nanoparticles synthesis using plant extract is a very effective synthesis process at a very reasonable cost. Recently, many reports have discussed the successful synthesis of iron nanoparticles via green chemistry (Badmapriya and Asharani, 2016; Kanagasubbulakshmi and Kadirvelu, 2017).

Iron nanoparticles (INPs) are among the most interesting novel materials. Due to their unique physicochemical properties, high catalytic activity, high magnetism, low toxicity, and microwave absorption ability (Hubar, 2005; Guo *et al*., 2012) .

4. Conclusion

The results of the present investigation clearly demonstrates that the mode of synthesis determines the structure, size, chemistry of the resultant nanoparticles. The newly synthesized iron nanoparticles are highly stable and it is reasonable to infer that the biomolecules of *Cassia auriculata* provides the property.

Reference

1. Khan, K. Saeed, I. Khan, Nanoparticles: properties, applications and toxicities, Arab J Chem. 12, 908e931 (2019); https://doi.org/10.1016/j.arabjc.2017.05.11.
2. L. Aakash, B.S. Vinduja, T. Arunkumar, T. Sivakumar, D. Gajalakshmi, A systematic review on green synthesis ofnanoparticles and its medical applications, *J Xidian Univ*. 14, 069e6076 (2020); https://doi.org/10.37896/jxu14.8/084.
3. H.D. Yu, M.D. Regulacio, E. Ye and M.Y. Han, Chemical routes to top-down nanofabrication, *Chem Soc Rev*. 42, 6006e6018 (2013); DOI: 10.1039/C3CS60113G.
4. R. Singh and J. Lillard Jr, Nanoparticlebased Targeted Drug Delivery, *Exp. Mol. Pathol*., 86, 215–223 (2009); doi: 10.1016/j.yexmp.2008.12.004.
5. H. Ijas, I. Hakaste, B. Shen, M.A. Kostiainen and V. Linko. Reconfigurable DNA origami nanocapsule for pH-controlled encapsulation and display of cargo. *ACS Nano*, 13, 5959-5967 (2020); doi: 10.1021/acsnano.9b01857.
6. E. Della Gaspera, S.P. Ratnayake, J. Ren, E. Colusso, M. Guglielmi and A. Martucci. SILAR deposition of metal oxide nanostructured films. *Small*, 17 (2021); doi: 10.1002/smll.202101666.
7. J. Kudr, Y. Haddad, L. Richtera, Z. Heger, M. Cernak, V. Adam, O. Zitka, Magnetic nanoparticles: from design and synthesis to real world applications, *Nanomaterials*, 7, 1e29, (2017); https://doi.org/10.3390/nano7090243.
8. K.S. Siddiqi, A. ur Rahman, Tajuddin, A. Husen, Biogenic fabrication of iron/iron oxide nanoparticles and their application, *Nanoscale Res Lett*, 11, 498 (2016); https://doi.org/10.1186/s11671-016-1714-0.
9. S. Bayda, M. Adeel, T. Tuccinardi, M. Cordani, F. Rizzolio, The history of nanoscience and nanotechnology: from chemical-physical applications to nanomedicine, *Molecules*., 25 (2020) 1e15, https://doi.org/10.3390/molecules25010112.
10. R. Brayner, F. Fi´evet, and T. Coradin, Synthesis of organic and bioorganic nanoparticles: an overview of the preparation methods, *Nanomaterials: A Danger or a Promise?AChemicaland Biological Perspective, J. Allouche, Ed.,* 27–74, (2013);
11. D. Mandal, M.E. Bolander, D. Mukhopadhyay, G. Sarkar and P. Mukherjee. The use of

microorganisms for the formation of metal nanoparticles and their application. *Appl. Microbiol. Biotechnol*. 69, 485-492 (2006); doi: 10.1007/s00253-005-0179-3.

12. Jebali, F. Ramezani and B. Kazemi. Biosynthesis of silver nanoparticles by *Geotricum sp*. *J. Clust. Sci*. 22, 225-232 (2011); http://dx.doi.org/10.1007/s10876-011-0375-5.
13. B.G. E. Hoag, J. B. Collins, J. L. Holcomb, J.R. Hoag, M.N. Nadagouda, and R.S. Varma. Degradation of bromothymol blue by 'greener' nano-scale zero-valent iron synthesized using tea polyphenols. *J. Mater. Chem.* 19, 8671-8677(2009); http://dx.doi.org/10.1039/B909148C.
14. T. Shahwan, S. Abu Sirriah, M. Nairat, E. Boyacı, A.E. Ero˘ glu, T.B. Scott and K.R. Hallam. Green synthesis of iron nanoparticles and their application as a fenton-like catalyst for the degradation of aqueous cationic and anionic dyes. *Chem. Eng. J.*, 172, 258–266 (2011); doi: 10.1016/j.cej.2011.05.103.
15. B. Z. Markova, P. Novak, J. Kaslik, P. Plachtova, M. Brazdova, D. Jancula, K.M. Siskova, L. Machala, B. Marsalek and R. Zboril. Iron(II,III)—Polyphenol complex nanoparticles derived from green tea with remarkable ecotoxicological impact. *ACS Sustain. Chem. Eng.*, 2, 1674–1680 (2014); http://dx.doi.org/10.1021/sc5001435.
16. D.M.N. Nadagouda, A.B. Castle, R.C. Murdock, S.M. Hussain, and R.S. Varma, In vitro biocompatibility of nanoscale zerovalent iron particles (nZVI) synthesized using tea polyphenols. *Green Chem.* 12, 114–122 (2010); http://dx.doi.org/10.1039/B921203P.
17. A. Bharde, R. Y. Parikh, M. Baidakova, S. Jouen, B. Hannoyer, T. Enoki, B.Prasad, Y.S. Shouche, S. Ogale and M. Sastry. Bacteria-mediated precursor-dependent biosynthesis of superparamagnetic iron oxide and iron sulfide nanoparticles. *Langmuir*. 24, 5787-5794 (2008); doi: 10.1021/la704019p.
18. J. W. Moon, C. J. Rawn, A. J. Rondinone, L. J. Love, Y. Roh, S. M. Everett, R. J. Lauf and T. J. Phelps. Large-scale production of magnetic nanoparticles using bacterial fermentation. *J. Ind. Microbiol. Biotechnol.* 37, 1023-1031 (2010); http://doi.org/10.1007/s10295-010-0749.
19. D.F. Luo, Z. Chen, M. Megharaj and R. Naidu. Biomolecules in grape leaf extract involved in one-step synthesis of iron-based nanoparticles. *RSC Adv.* 4, 53467–53474 (2014);
20. http://dx.doi.org/10.1039/C4RA08808E.
21. A.R. Herrera-Becerra, J. L. Rius and C. Zorrilla. Tannin biosynthesis of iron oxide nanoparticles. *Appl. Phys. A.* 100, 453-459 (2010); http://dx.doi.org/10.1007/s00339-010-5903.
22. S. Iravani. Green synthesis of metal nanoparticles using plants. *Green Chem*. 13, 2638–2650 (2011); doi: 10.1039/C1GC15386B.
23. G.L.Huang, X. Weng, Z. Chen, M. Megharaj and R. Naidu. Synthesis of iron-based nanoparticles using Oolong tea extract for the degradation of malachite green. *Spectrochim. Acta A.* 117, 801–804 (2013); http://doi.org/10.1016/j.saa.2013.09.054.
24. T. Maliar, J. Bozenko, H. Cesiulis and I. Prosycevas. Electrochemical aspects of the synthesis of iron particles. *Mater. Sci.* 18, 223–227 (2012); http://dx.doi.org/10.5755/j01.ms.18.3.2429.
25. S. Rashmi, G. Madhu, A. Kittur, and R. Suresh. Synthesis, characterization and application of zero valent iron nanoparticles for the removal of toxic metal hexavalent chromium from aqueous solution. *Int. J. Curr. Eng. Technol.* 37–42 (2013); http://inpressco.com/category/ijcet.
26. S. Kanagasubbulakshmi and K. Kadirvelu. Green synthesis of iron oxide nanoparticles using lagenaria siceraria and evaluation of its antimicrobial activity. *Def. life Sci. J.* 2, 422–427 (2017); http://doi.org/10.14429/dlsj.2.12277.
27. D. Badmapriya, I.V. Asharani. Dye degradation studies catalysed by green synthesized iron oxide nanoparticles. *Int. J. ChemTech Res*. 9, 409–416 (2016).
28. D.L. Huber. Synthesis, properties, and applications of iron nanoparticles. *Small Weinheim an der Bergstrasse, German, 1*(5), 482–501 (2005); doi: 10.1002/smll.200500006.
29. D.J. Guo, R. Wang, W.W. Tjiu, J. Pan and T. Liu. Synthesis of Fe nanoparticles@ graphene composites for environmental applications. *Journal of Hazardous Materials, 225*, 63–73 (2012);
30. doi: http://dx.doi.org/10.1016/j.jhazmat.2012.04.065.