POLİTEKNİK DERGİSİ

JOURNAL of POLYTECHNIC

ISSN: 1302-0900 (PRINT), ISSN: 2147-9429 (ONLINE)
URL: http://dergipark.org.tr/politeknik

Effect of lemon peel extract concentration on nano scale Fe/Fe_3O_4 synthesis

Limon kabuğu ekstratı konsantrasyonunun nano ölçekli Fe/Fe_3O_4 sentezine etkisi

Yazar(lar) (Author(s)): *Tuğçe AYDOĞAN[1], F. Tuğçe ŞENBERBER DUMANLI[2], Emek MÖRÖYDOR DERUN[3]*

ORCID[1]: 0000-0002-8934-5931

ORCID[2]: 0000-0002-3257-1524

ORCID[3]: 0000-0002-8587-2013

Bu makaleye şu şekilde atıfta bulunabilirsiniz(To cite to this article): Aydoğan T., Dumanlı F. T. ve Derun E., "Effect of lemon peel extract concentration on nano scale Fe/Fe_3O_4 synthesis", ***Politeknik Dergisi***, 25(4): 1423-1427, (2022).

Erişim linki (To link to this article): http://dergipark.org.tr/politeknik/archive

DOI: 10.2339/politeknik.938200

Effect of Lemon Peel Extract Concentration on Nano Scale Fe/Fe_3O_4 Synthesis

Highlight

- *Nanoparticles synthesized without using pH agent or stabilizer.*
- *Lemon peel extract performed as a capping agent to modify the morphology and particle size.*
- *The smallest particle size was measured between 66.68 and 156 nm for Fe:Lemon peel extract ratio of 1:2.*

Graphical Abstract

The effect of lemon peel extract on characteristic properties of iron-iron oxide nanoparticle was studied.

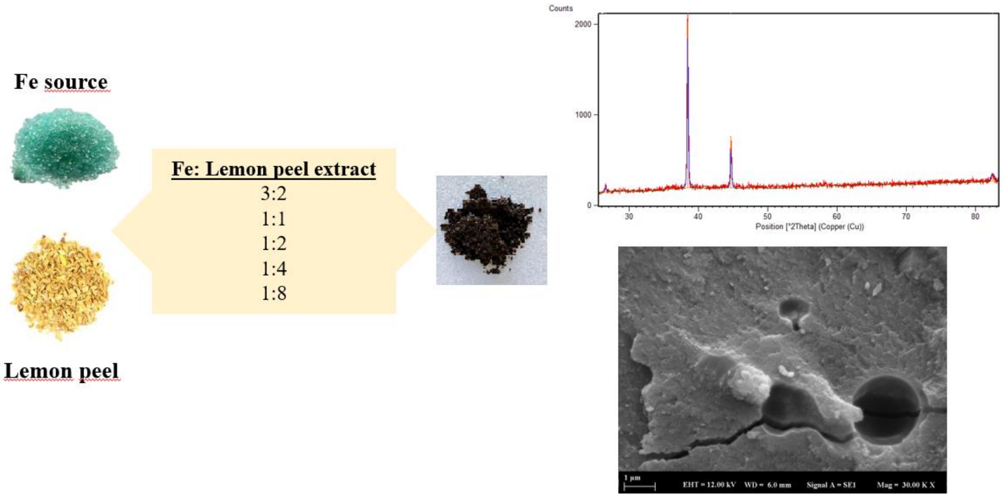

Figure. Synthesis procedure scheme

Aim

This study aimed to synthesis Fe-Fe_3O_4 nanoparticles with lemon peel extract without using any stabilizer.

Design & Methodology

Different stoichometric ratios of iron sulphate and lemon peel extract were reacted and characterized by using, XRD, UV-Vis spectroscopy and SEM.

Originality

By using lemon peel extract as a capping agent, Fe-Fe_3O_4 nanoparticles were synthesized without using any stabilizer.

Findings

The UV-vis absorption spectrum of iron nanoparticles showed a peak in the 250-350 nm range. XRD analysis results confirmed that the product is a Fe-Fe_3O_4 mixture. For the optimum ratio (1:2), the particle size range was found between 66.68 and 159 nm.

Conclusion

It has been determined that Fe-Fe_3O_4 particles can be synthesized in nano scale with lemon peel extract. In addition; it can be performed without the need for a stabilizer or modification agent for synthesis.

Declaration of Ethical Standards

The authors of this article declare that the materials and methods used in this study do not require ethical committee permission and/or legal-special permission.

Effect of Lemon Peel Extract Concentration on Nano Scale Fe/Fe_3O_4 Synthesis

Araştırma Makalesi / Research Article

Tuğçe AYDOĞAN[1], F. Tuğçe ŞENBERBER DUMANLI[2], Emek MÖRÖYDOR DERUN[1*]

[1]Faculty of Chemical and Metallurgical Engineering, Department of Chemical Engineering, Yıldız Technical University, Turkey
[2]Faculty of Engineering and Architecture, Department of Civil Engineering, Nişantaşı University, Turkey

(Geliş/Received : 17.05.2021 ; Kabul/Accepted : 30.05.2021 ; Erken Görünüm/Early View : 01.06.2021)

ABSTRACT

Iron nanoparticles has attracted more attention than other nanomaterials for its small particle size, high magnetism, low toxicity, surface properties and its extensive applications in science. Plant extracts, microorganisms and agricultural waste products are used for the green synthesis of these nanoparticles. Green synthesis uses metabolites obtained from plants and microorganisms as reducing and covering agents. In addition, it provides an advantage over other synthesis methods because it does not contain harsh chemicals, uses non-toxic reagents, is biocompatible and environmentally friendly. In this study, iron-iron oxide (Fe-Fe_3O_4) nanoparticles (LP- Fe NPs) were synthesized using lemon peel extract and optimum Fe:Lemon peel extract (Fe: LP exract) ratio was determined. Nanoparticles were characterized by X-ray diffractometer (XRD), UV-vis Spectrophotometer and Scanning Electron Microscope (SEM). The UV-vis absorption spectrum of iron nanoparticles showed a peak in the 250-350 nm range. XRD analysis results confirmed that the product is a Fe-Fe_3O_4 mixture. According to SEM analysis results, the largest particle size according to the 1:2 ratio was recorded as 159 nm. The smallest particle size was recorded as 66.68 nm. It has been observed that the increased lemon peel extract causes agglomeration. As a result, green synthesis of lemon peel, which is agricultural waste; It creates low-cost, environmentally friendly products.

Keywords: **Green synthesis, morphology, nanomaterial, iron nanoparticle, lemon peel.**

Limon Kabuğu Ekstratı Konsantrasyonunun Nano Ölçekli Fe/Fe_3O_4 Sentezine Etkisi

ÖZ

Demir nanopartiküller; küçük partikül boyutu, yüzey özellikleri, düşük toksisitesi, yüksek manyetizması ve bilimdeki kapsamlı uygulamaları nedeniyle diğer nanomalzemelere göre daha fazla ilgi çekmiştir. Bu nanopartiküllerin yeşil sentezi için bitki özleri, mikroorganizmalar ve tarımsal atık ürünler kullanılmaktadır. Yeşil sentez, bitkilerden ve mikroorganizmalardan elde edilen metabolitleri indirgeyici ve kapatıcı ajanlar olarak kullanır. Ayrıca sert kimyasallar içermemesi, toksik olmayan reaktiflerin kullanılması, biyouyumlu ve çevre dostu olması nedeniyle diğer sentez yöntemlerine göre avantaj sağlamaktadır. Bu çalışmada, demir-demir oksit (Fe-Fe_3O_4) nanopartikülleri limon ekstratı kullanılarak sentezlenmiş ve optimum Fe:Ekstrakt oranı belirlenmiştir. Nanopartiküller, X-ışını difraktometresi (XRD) , UV-vis Spektrofotometre ve Taramalı Elektron Mikroskobu (SEM) ile karakterize edilmiştir. Demir nanopartiküllerinin UV-vis absorpsiyon spektrumu 250-350 nm aralığında bir tepe göstermiştir. XRD analiz sonuçları, ürünün bir Fe-Fe_3O_4 karışımı olduğunu doğrulamıştır. SEM analizi sonuçlarına göre 1: 2 (Fe:Ekstrat) oranında en büyük partikül boyutu 159 nm olduğu görülürken, en küçük partikül boyutu 66.68 nm olarak kaydedilmiştir. Artan limon özünün topaklaşmaya neden olduğu gözlenmiştir. Sonuç olarak, tarımsal atık olan limon kabuğunun yeşil sentezi düşük maliyetli, çevre dostu ürünler oluşturmaktadır.

Anahtar Kelimeler: Demir nanopartikül, limon kabuğu, morfoloji, nanomateryal, yeşil sentez.

1. INTRODUCTION

Citrus varieties are one of the products grown around the world. Citrus cultivation is in a rapid development process both in the world and in our country. Turkey with 4.902.052 tones took seventh place among the largest citrus producing countries in the year 2018 [1]. In 2018, the total citrus production in some regions of Turkey are as follows; 88.04% the Mediterranean, 11.54% the Aegean, 0.20% the West Marmara, 0.08 % the Black Sea and 0.14% the Southeastern Anatolia Region [2]. Citrus fruits have wide economic and pharmaceutical importance to their rich macro and micronutrient content. Analyses on citrus fruits helped to identify biologically active ingredients, including flavonoids and alkaloids [3]. Nanoparticles, defined as microscopic particles smaller than 100 nm in size, are classified as advanced materials in nanotechnology. Because of the properties they have, they are preferred mainly in thermal, electrical, chemical, optical, medical, agriculture, information and communication technologies. Nanoparticles can be produced by modifying the material with physical and chemical techniques to produce a material with specific properties useful in many applications [4]. Iron nanoparticles differ from other types of nanoparticles due to their small particle size, surface properties, non-toxic content and high magnetism [5]. Plant extracts, microbes and agricultural waste products are used in the green

**Sorumlu Yazar (Corresponding Author)*
e-posta : moroydor@yildiz.edu.tr

synthesis of these nanoparticles. Thus, it is aimed to increase the synthesis efficiency and decrease the cost [6, 7].

Various methods such as co-precipitation method, chemical reduction method, sol-gel method and hydrothermal synthesis method are available for the synthesis of nanomaterials [12]. It has been observed that nanoparticles produced by these methods, together with the chemicals used for production, harm the environment. Thus, the production of nanomaterials with green synthesis method was preferred. Green synthesis method differs from other synthesis methods today due to its features such as being economically feasible, simple and environmentally friendly. Magnetic nanoparticles synthesized by this method do not show toxic properties compared to nanoparticles synthesized using $NaBH_4$ [13]. The plant extract used in nanoparticles synthesized by the green synthesis method functions both as a capping and a reducing agent [14]. It has been reported by many researchers that fruit peels are used in the green synthesis of iron nanoparticles such as; Citrus paradise peel [15], Citrus maxima peel [16], Citrus sinensis (L.), Citrus limettioides Tan, Citrus limon (L.) and Citrus reticulata [17].

As a food waste, the use of lemon peel would contribute to the solution of the environmental waste problem in terms of not applying any pre-treatment to the raw material and provided the economic benefit of the production. Not using harmful and toxic chemicals such as $NaBH_4$ in the production of particles synthesized with an environmentally friendly approach is defined as an innovative approach. As a result of the experimental studies, iron nanoparticles were produced with the help of lemon peel extract without the need for any toxic chemicals and it was aimed to determine the optimum Fe: Lemon peel extract ratio.

2. MATERIAL AND METHOD

2.1. Preparation of Peel Extract of Lemon

Lemon (Citrus) used in the experiments was obtained from Mersin/ Erdemli region. Lemon peels (LP), which have been washed three times beforehand, are cut into the homogeneous sizes. The prepared lemon peels were extracted in pure water at 75 ºC for 1 hour. The obtained light-yellow extract was filtered through blue filter paper and stored at 4 °C.

2.2. Green Synthesis of LP- Fe NPs

Iron sulphate heptahydrate ($FeSO_4.7H_2O$, purity of % 99.5) used as the Fe source was supplied from Merck (Darmstadt, Germany) and a 0.1 M solution was used. For the synthesis of iron nanoparticles, Fe: LP extract ratios were determined as 3: 2, 1: 1, 1: 2, 1: 4, 1: 8. The prepared solutions were reacted at 80 ºC for 1 hour in a magnetic stirrer. The color change of the mixture of Fe solution and lemon peel extract from yellow to black confirmed the iron nanoparticle formation [18]. The prepared samples were filtered with blue filter paper and dried in an oven (Ecocell 111, Germany) at 105 ºC for 12 hours.

2.3. Characterization Experiments of LP- Fe NPs

UV-vis spectroscopy, X-ray diffractometer (XRD) and Scanning electron microscopy (SEM) were used to characterize the synthesized LP- Fe NPs. The samples were verified by using PANalytical X'pert Pro XRD (PANalytical B.V., Almelo, The Netherlands). The details of the parameters used in the XRD analysis were Cu-Kα tube (λ =0.153 nm) , voltage of 45 kV ,step size 0.03°, step time 0.5 s, current of 40 mA, scan speed of 0.06 °C/s, and scan range of 40–85. Perkin Elmer UV-Vis spectrophotometer was used for the analysis of characteristic bands for the Fe atom in the 190-1100 nm range. The samples are dissolved in water for use in UV analysis. ZEISS EVO LS 10 model SEM (ZEISS EVO LS 10, Germany) was used to examine the morphology of the samples. The backscattered electron detector was used in this analysis at 30000X magnification.

3. RESULT AND DISCUSSION

3.1. Possible Mechanism of Reduction

The images of prepared samples can be seen in Figure 1. The black color of samples at the ratios of 1:2, 1:4 and 1:8 could indicate the possible complex formation of Fe and Fe_3O_4. The light-colored powder formation can be explained with the unreacted amount of iron sulphate heptahydrate.

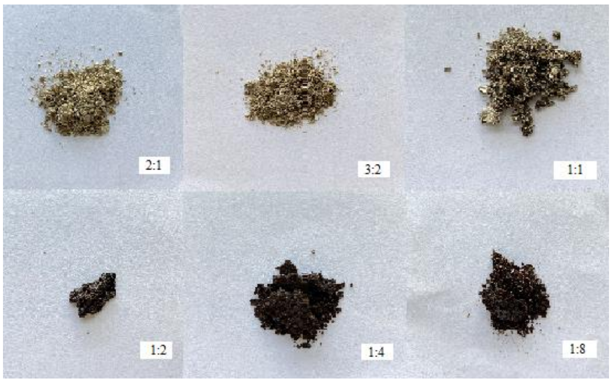

Figure 1. Images of prepared samples at different ratios

Particle growth in solution takes place in two basic steps: diffusion from the bulk to the particle surface and binding reaction between ion - solid particle [19]. The possible reaction mechanism of Fe and Fe_3O_4 complexes can be explained with the following steps:

(i)Formation of FeO(OH) complex with the hydrolysis of $FeSO_4.7H_2O$

(ii)Transform of FeO(OH) particles to Fe and Fe_3O_4 complexes

(iii)Particle size adjustment by adding lemon peel extract as capping agent.

3.2. UV-vis Analysis

UV-vis spectroscopy is a fast and simple method for the characterization of iron nanoparticles as well as an important technique for the formation of nanoparticles [20]. The UV-vis spectra of lemon and ferrous sulphate heptahydrate used in the synthesis were presented in Figure 2. Ferrous sulphate heptahydrate ($FeSO_4.7H_2O$) used as the iron source exhibited an absorption peak between 250-270 nm in Uv- vis spectroscopy. The lower band values than 250 nm for lemon peel extract can be explained with the citric acid content of sample [21].

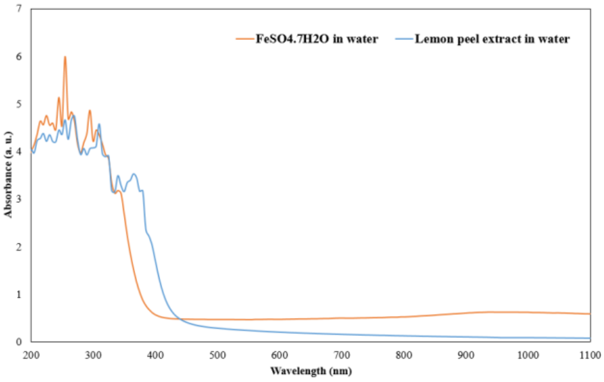

Figure 2. UV- vis absorption peak Lemon peel exctract and $FeSO_4$. $7H_2O$

UV visible spectroscopy of iron nanoparticles is observed in the 250-350 nm range [20]. In Figure 3, Uv-vis spectroscopy absorption peaks of Fe:LP extract ratio scanning in solution are presented. The weak peaks range in the 250-350 nm were obtained in products with Fe: LP extract ratio of 2:1, 3:2, 1:1, respectively. The strong peaks around 250-350 nm were obtained in products with Fe:LP extract ratio of 1:2, 1:4 ,1:8. This situation can be interpreted with the positive effect of increasing lemon peel extract rate on nanoparticle formation. However, the peak around 220 nm at the ratio of 1:2, 1:4,1: 8 can be interpreted with the citric acid content of lemon. According to the Figure 3, the ratio of 1:2 was selected as optimum.

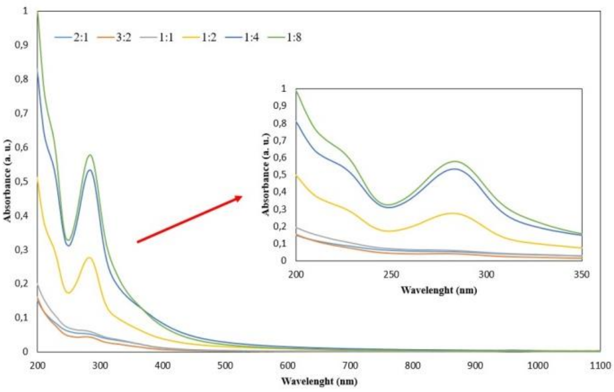

Figure 3. UV–vis absorption peak of LP- Fe NPs

3.2. SEM Analysis

According to the SEM analyses, SEM morphologies can be seen in Figure 4 and particle size distribution for different Fe: LP extract ratios is given in Table 1. The results indicated that the increase of lemon peel extract in solution medium reduced the particle sizes. The close contact of iron nanoparticles is attributed to the magnetic properties of the iron species as reported by Feng and Lim [18]. Minor changes were obtained in particles sizes at the ratios less than 1:2. However, agglomeration of particles was observed at the ratio of 1:4 and 1:8. According to the SEM results, the optimum ratio was selected as 1:2.

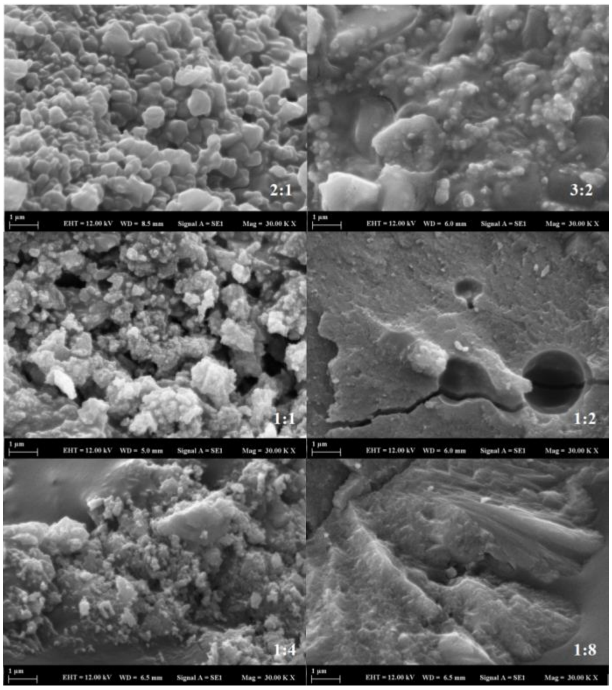

Figure 4. SEM images of samples prepared with different Fe:LP extract ratios

Table 1. Particle size analysis of different Fe:LP extract ratios

Fe: Extract	Particle size range (nm)
2:1	938-339
3:2	425-250
1:1	172-84
1:2	159-67
1:4	227-52
1:8	114-47

3.3. XRD Analysis

The XRD pattern of LP- Fe NPs, synthesized at different ratios, was presented in Figure 5. According to the results, the mixture of Fe, Fe_3O_4 and FeO(OH) were observed at the ratios of 2:1 and 3:2. The mixture of Fe and FeO(OH) were determined at the ratio 1:1. The samples synthesized at the ratios of 1:2, 1:4 and 1:8 were identified as the zero valent Fe. The peak at 45^o corresponds to α-Fe [18] and the higher percentages of lemon peel extract affected positively the peak formation 45°. The black-colored samples were identified as a mixture of Fe, FeO(OH) and Fe_3O_4 with a powder diffraction file number “01-089-7194”, “00-022-0353” and “01-089-6466” respectively. Therefore, it has been confirmed that the synthesized nanoparticles contain zero valence iron nanoparticles together with iron oxide.

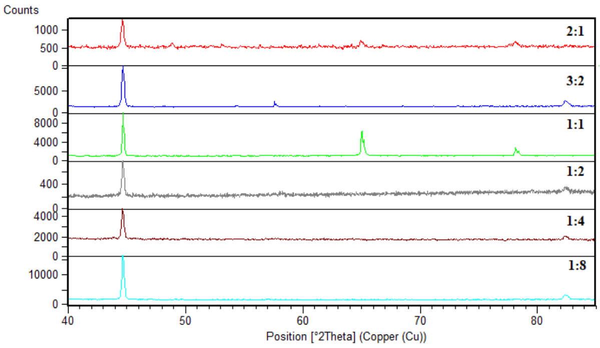

Figure 5. XRD pattern of LP- Fe NPs synthesized at different ratios

4. CONCLUSION

The mixture of Fe/Fe_3O_4 nanoparticles were synthesized successfully from $FeSO_4.7H_2O$ and lemon peel extract without using any stabilizer, pH agent or modifying agent. In this procedure, lemon peel extract was determined as capping agent to modify the surface of synthesized particles. The positive effects of lemon peel extract addition on Fe formation was determined in XRD analyses. However, the band values in the range of 200 - 250 nm in UV- Vis spectrum indicated the excess amounts of citric acid. According to the characterization results, the Fe: Extract ratio of 1:2 was selected as optimum. The mixture of Fe/Fe_3O_4 nanoparticles was identified with XRD analyses. In this study, the use of lemon peel was beneficial in recycling the peeling waste and provided an economic benefit. The obtained data indicated that the use of lemon peel extract in iron and iron oxide nanoparticle synthesis would contribute the green synthesis procedures in literature.

ACKNOWLEDGEMENTS

This research was supported by the Coordination Unit for Scientific Research Projects, Yıldız Technical University. (Project No: FYL-2021-4130)

DECLARATION OF ETHICAL STANDARDS

The authors of this article declare that the materials and methods used in this study do not require ethical committee permission and/or legal-special permission.

AUTHORS’ CONTRIBUTIONS

Tuğçe AYDOĞAN: Performed the experiments.

F. Tuğçe ŞENBERBER DUMANLI: Analysed the data.

Emek MÖRÖYDOR DERUN: Designed the study.

CONFLICT OF INTEREST

There is no conflict of interest in this study.

REFERENCES

[1] **http://www.fao.org/faostat/en/#data/QC**, “Food and Agriculture Organization (FAO), 2018 Production Data”, Available from:, Date of access: 06.03.2021

[2] Kurt Ş. “Batı akdeniz tarımsal araştırma enstitüsü Türkiye turunçgil çeşit geliştirme programı”, ***T.C. Tarım ve Orman Bakanlığı Tarımsal Araştırmalar ve Politikalar Genel Müdürlüğü Batı Akdeniz Tarımsal Araştırma Enstitüsü***, Antalya, 1-10, (2020).

[3] Raghavan S., Gurunathan J., “Citrus Species- a Golden Treasure box of metabolites that is beneficial against disorders”, ***Journal of Herbal Medicine***, 28 : 100438, (2021).

[4] Hanif M., Nazri M., Sapawe N., “A short review on green synthesis of iron metal nanoparticles via plants extracts”, ***Materials Today Proceddings***, 31: A48-A53, (2020).

[5] Frey N.A., Sun S., “**Magnetic Nanoparticle for Information Storage Applications**” ,Inorganic nanoparticles: synthesis, applications, and per-spective, *Taylor and francis group*. ,USA, (2011).

[6] Ebrahiminezhad A., Davaran S., Rasoul-Amini S. , et al., “Synthesis, characterization and anti-listeria monocytogenes effect of amino acid coated magnetite nanoparticles”, ***Current Nanoscience,.*** 8 (6): 868-874, (2012).

[7] Ebrahiminezhad A., Barzegar Y., Ghasemi Y., et al., “Green synthesis and characterization of silver nanoparticles using Alcea rosea flower extractas a new generation of antimicrobials”, ***Chemical Industry and Chemical Engineering Quarterly.***, 23 (1): 31-37, (2017).

[8] Mahakham W. , Theerakulpisut P., Maensiri S., et. al,”Environmentally benign synthesis of phytochemicals-capped gold nanoparticles as nanopriming agent for promoting maize seed germination”, ***Science of Total Environment***. 573 : 1089-1102, (2016).

[9] Xu P., Zeng G.M.,. Huang D.L., et al., “Use of ironoxide nanomaterials in waste water treatment: a review”, ***Science of Total Environment*** ,424 : 1-10, (2012).

[10] Ehrampoush M.H., Miria M., Salmani M.H., et al., “Cadmium removal from aqueous solution by green synthesis iron oxide nanoparticles with tangerine peel extract”, ***Journal of Environmental Health Science and Engineering.***, 13(84): 1-7, (2015).

[11] Khalil A., Ovais M., Ullah I., et al., “Biosynthesis of iron oxide (Fe_2O_3) nanoparticles via aqueous extracts of Sageretia thea (Osbeck.) and their pharmacognostic properties”, ***Green Chemistry Letters Reviews.*** 10:186-201, (2017).

[12] Ahmed, E.M., “Hydrogel: preparation, characterization, and applications: a review”.***Journal of Advanced Research*** ,6: 105–121, (2015).

[13] Bhuiyan M. , Miah M., Paul S. et al.,“Green synthesis of iron oxide nanoparticle using Carica papaya leaf extract:application for photocatalytic degradation of remazol yellow RR dye and antibacterial activity”; ***Heliyon***, 6 (e04603): 1-13, (2020).

[14] Peralta-Videa J.R., Huang, Y., Parsons, J.G.,et al., “Plant-based green synthesis of metallicnanoparticles: scientific curiosity or a realistic alternative to chemical

synthesis" , ***Nanotechnology for Environmental Engineering volume*** , 1 : 1–29, (2016).

[15] Kumar B., Smita K., Galeas S., "Characterization and application of biosynthesized iron oxide nanoparticlesusingCitrus paradisipeel: A sustainable approach", ***Inorganic Chemistry Communications***,119 :108116 , (2020).

[16] Wei Y., Fang Z., Zheng L., "Green synthesis of Fe nanoparticles using Citrus maxima peels aqueous extracts", ***Materials Letters***, 185: 384–386, (2016).

[17] Machado S., Grosso J.P., Nouws H.P.A., "Utilization of food industry wastes for the production of zero-valentiron nanoparticles", ***Science of the Total Environment***, 496: 233–240 , (2014).

[18] Jain R., Mendiratta S., Kumar L., Srivastava A., 456–89, "Green synthesis of iron nanoparticles using Artocarpus heterophyllus peel extract and their application as a heterogeneous Fenton-like catalyst for the degradation of Fuchsin Basic dye", ***Current Research in Green and Sustainable Chemistry***, 4: 100086, (2021).

[19] Phan C M, Nguyen H. M., "Role of Capping Agent in Wet Synthesis of Nanoparticles" ***Journal Of Physical Chemistry A***, 121: 3213−3219, (2017).

[20] Sadhasivam S., Vinayagam V., Balasubramaniyan M., "Recent advancement in biogenic synthesis of iron nanoparticles", ***Journal of Molecular Structure*** 1217: (128372): 1-8, (2020).

[21] Mohan, S., Singh, Y., Verma, D., Hasan, S., "Synthesis of CuO nanoparticles through green route using Citrus limon juice and its application as nanosorbent for Cr(VI) remediation: Process optimization with RSM and ANN-GA based model", ***Process Safety and Environmental Protection***, 96: 156 – 166, (2015).