Preparation of Iron nanoparticles using plant extract

For

Masters of Science (Hons.) in chemistry

Lovely Professional University

Phagwara, Punjab

By

Arunmeet kaur (Regd. No. 11511974)

Under the supervision

Of

Dr. Runjhun Tandon

Assistant Professor

Department of Chemistry

ACKNOWLEDGEMENT

I would like to express my sincere gratitude to my supervisor **Dr. Runjhun Tandon** and respected H.O.D. **Dr. Ramesh Chand Thakur** who gave me the golden opportunity to do this project on the topic **"Preparation of Iron nanoparticles using plant extract".** The guidance of my supervisor has opened the research pursuit which was residing deep in my mind in the last three months. With his timely guidance I came to know so many new things related to latest advancements the field of nanotechnology. I am highly thankful to them. Secondly I would like to thank my parents and friends who helped me so wisely in finalizing my project within a limited time.

Certificate

I have immense pleasure in forwarding the capstone project research work of **Ms. Arunmeet kaur** (Reg. No. 11511974) entitled **"Synthesis of nanoparticles of Iron using plant extract"** is in partial fulfillment of the requirements for the award of the degree of Master in Hons Science in Chemistry registered at Lovely Professional University, Phagwara, Punjab.

It is certified that Ms. Arunmeet kaur has investigated the problem under my guidance and supervision with diligence and in the concerned manner. The work embodied in this capstone project is original and has not been submitted in full or in part, for any other degree in this work or other Institute/University.

Dr. Runjhun Tandon

Table of contents:-

Introduction

In modern field of science, nanotechnology is one of the most active field for research. Richard Feynman is known as the father of nanotechnology. The nanotechnology field has a very impressive development in past few years. Various methods are developed for the synthesis of metal nanoparticles. Because of their Nano size the properties of metals like functionality, biological properties, improved physical and chemical properties. Nanoparticles are efficiently a bridge between bulk material and atomic or molecules due to this nanoparticles are of great scientific interest. As the material reaches to nano scale its properties also changes. The interesting and sometimes unexpected properties of nanoparticles are not partly due to the aspects of the surface of the material dominating the properties in lieu of the bulk properties. Nanoparticles exhibit a number of special properties relative to bulk material. Particles of metal oxide of size less than 100 nm are considered as Nano sized particles and also used as precursors for the synthesis of new materials. Nano particles of metal oxides are of great interest. They have a characteristic properties and application in various fields. The properties of metal oxides nano particles are depend upon the size of nano particles. Some of the applications of nano particles are carbon nanotubes, fullerenes, nanopolymers, nanomembranes, nanocatalysts, nanoformulations for cosmetics, nanoceramics etc. Nanoparticles also have applications in various fields such as semiconductors, fuel cells, solar cells, agriculture, in therapeutic, drug delivery etc. Nanoformulations are of great use in cosmetics and dermal patches for drug delivery.

Many harmful chemicals and gasses are released by the industries due to industrialization and urbanization which is destroying our environment day by day. So we should reveal the secrets of nature so as they are eco-friendly and it will lead the advancements of green synthesis in the field

of synthesis of nano particles. Nanoparticles have exclusive properties due to which they are suitable for biological molecules. The biological molecules require highly controlled assembly for which make them suitable for the metal nanoparticle synthesis making them reliable and eco-friendly [1]. The vast area of research now a days is synthesis of metal and semiconductor due to their potential applications which was useful for the development of novel technologies [2]. New and improved properties are shown by the nanoparticles such as morphology of the particle and size distribution etc. Novel applications of nanomaterials and nanoparticles are increasing rapidly on various fields [3].

Surface area of nano particle is very high and has high fraction of surface atoms. Nanoparticles possess many properties like optical properties, electronic properties, antibacterial properties, catalytic activity and magnetic properties due to its unique physiochemical properties that's why they are seeking interest of the scientists for novel methods of synthesis.

At present there is an emergent need of development of synthesis routes of nanoparticles which are environmental friendly. Many ecological materials can be used like bacterial cell extract, plants leave extract, fungi and enzymes for the synthesis of nanoparticles. Today, the synthesis of these nanoparticles are done by green synthesis using plant extract in many industries and scientific research [4]. Green synthesis plays a significant role in the synthesis of nanoparticles as the cost of production is low and less time consuming as compare to chemical methods. The use of different plants for the synthesis of nanoparticles is also beneficial for our environment. Also the chemicals that are used for the synthesis of nanoparticles are toxic and form many harmful by-products. Therefore the demand of "green synthesis" is increasing day by day.

A better platform for the synthesis of nanoparticles is provided by plants as they are non-toxic and easily available. The cost of microorganisms and to maintain their culture is very high so green synthesis is preferred over the use of microorganisms for the production of nanoparticles [5]. Many biological methods for the synthesis of nanoparticles involves the complex method for the maintenance of microbial culture so in that case nanoparticles are prepared by various plants and their extracts [6, 7].

REVIEW OF LITERATURE

Nanotechnology:-

Due to various applications in the field of medical science, technology and research areas, nanotechnology becomes a high developing field. The word ‘nano’ means very small in Greek language. Richard Feynman is known as the father of nanotechnology. The term “Nanotechnology” was later coined by Professor Norio Taniguchi by using Feynman’s explorations of ultra-precision machining. In 1974, the term nanotechnology was pioneered by Nori Taniguchi on the talk of Production Engineering at the Tokyo International Conference [8].

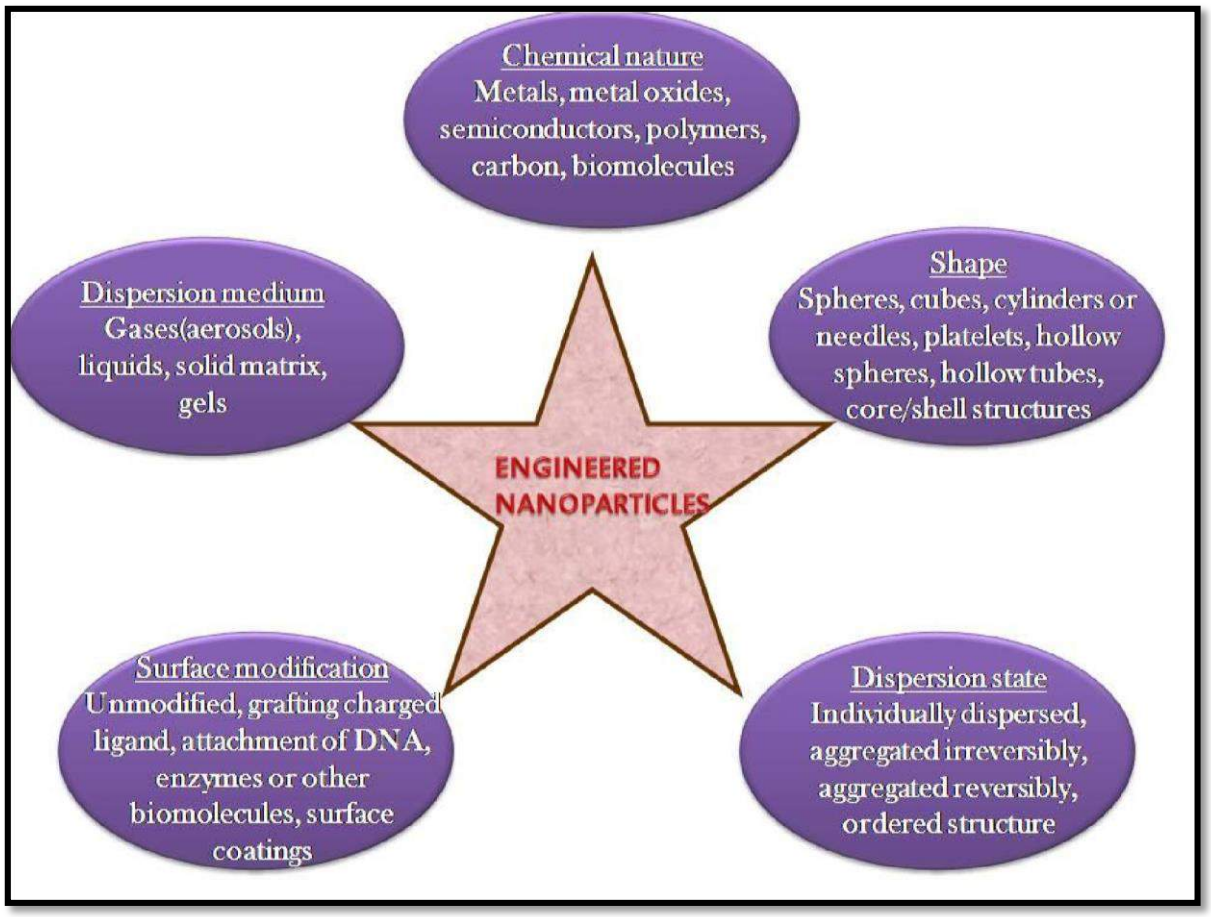
Nanoscience and nanotechnology provides a developed applications in the field of science and development like chemistry, material, physics, metallurgy engineering, and biology and in biotechnology also. [9] Bio nanotechnology is the conjunction between biotechnology and nanotechnology for developing various environmental eco-friendly and bio-synthetic technologies for the production of various nanomaterials [10].

The US National Science and Technology Council gives a brief definition of nanoparticles which states that “The essence of nanotechnology has the capability to work at the molecular level such as atom by atom for the creation of large structures with essentially innovative molecular organization. The aim is to exploit these properties by gaining control of structures and devices at atomic, molecular, and supra molecular levels and to become skilled at well-organized

manufacture and use these devices." The United States National Science Foundation (USNSF) defines nanotechnology [11] is the study which gives following properties:-

1. The particle size must be in the range of 1-100 nm.
2. The procedure of synthesis of nanoparticles can be designed in many ways and which show elementary control over the physical and chemical properties of structures that can be measure by the molecular-scale.
3. Large structures are formed by the combination of small structures this theory is according to building block property. According to microbiological study, different size of nanoparticles can be yield by using different types of bacteria, viruses and enzymes.

Nanotechnology has a great role in various fields like diagnostic drug delivery, sunscreens, antimicrobial bandages, diagnostic process, disinfectant and a friendly manufacturing process. Nanotechnology is also used for the removal of toxic wastes from water [12]. Nanotechnology is also used in food industries for the packing purpose of food. Antimicrobial packing of nanoparticles are done so as to protect the food from oxygen, carbon dioxide and from moisture which control the growth of microorganisms [13]. They have potential use as fungicides in agriculture, imaging in biomedical applications and as an anticancer drug.



Green synthesis of nanoparticles:-

A better platform for the synthesis of nanoparticles is provided by plants as they are non-toxic and easily available. . The cost of microorganisms and to maintain their culture is very high so green synthesis is preferred over the use of microorganisms for the production of nanoparticles [5]. Many biological methods for the synthesis of nanoparticles involves the complex method for the maintenance of microbial culture so in that case nanoparticles are prepared by various plants and their extracts [6, 7].

Nanoparticles of iron have many applications in the field of environmental remediation techniques. Many green routes are used for their synthesis by using various plants extract like Euphorbia milii, Tridax procumbens, Tinospora cordifolia, Datura innoxia, Calotropis procera and Cymbopogon citratus (lemon grass tea). $FeCl_3$ (ferric chloride) is used for the synthesis of nanoparticles of iron along with plant extract. The reductants present in plant extract is helpful for the stabilization and reduction of nanoparticles. The synthesized nanoparticles are characterized by using various techniques like transmission electron spectroscopy (TEM), XRD (X-ray diffraction), UV-vis spectroscopy, IR spectroscopy, particle size analyser, scanning electron spectroscopy (SEM) etc. These method of synthesis is eco-friendly, low cost, less time consuming therefore used for the production of nanoparticles at large scale [14].

Zero valent iron nanoparticles are also very useful as they are used to remove the pollutants present in soils and water. These zero valent nanoparticles of iron 10-1000 times more reactive than granular and micro-scale iron particles because they are more specific, small particle size and high reactivity. Zero valent iron nanoparticles are prepared by using green tea extract which is antioxidant. Polyphenols present in the green tea extract not only reduce the nanoparticles produce but also stabilize these nanoparticles [15].

Various biological processes are reported for the synthesis of nanoparticles but among all the nanoparticles which are prepared by plant extract are more preferred. This process of synthesis is not only eco-friendly but also economically favourable. Nepenthes khasiana has both medicinal and antibacterial properties which is use for the production of gold nanoparticles. The synthesised nanoparticles are then characterized by using UV-*vis* spectrophotometry, Scanning Electron Microscopy (SEM), Fourier Transform Infra-red Spectroscopy, XRD (X-ray diffraction) and Transmission Electron Microscopy [16].

Fe_2O_3 nanoparticles are also prepared by using peanut plant leaves and its characterization is done by using FT infrared spectroscopy. The nanoparticles of iron which are prepared by using green tea exact is also useful for the removal of malachite dye [17].

For the synthesis of silver and gold nanoparticles by using various plant extracts like cauliflower extract, papaya extract, Trianthema decandra root extract, Meringa oleifera leaf extract, Garcinia mangostana fruit extract, Aloe Vera extract, Argemone Mexicana extract, Artocarpus heterophyllus fruit extract, Nepenthes khasiana leaf extract**,** Ananas comosus fruit extract,

Mangosteen leaf extract etc. These nanoparticles are used in integrated circuits, sensors, textile industry, food industries, biolabeling filters, cell electrodes, low cost paper batteries, health industries and also used in environmental applications [18].

ZnO nanoparticles were successfully prepared by biological synthesis using aqueous extracts of Allium sativum (garlic), Allium cepa (onion) and Petroselinum crispum (parsley). The particle size is influenced by the type of plant extract used and varies between 14 and 70 nm. [19]

Copper oxide nanoparticles are also prepared by green synthesis using black bean plant extract which was further characterized by using techniques like XRD, FT-IR, Raman spectroscopy, TEM, SEM, and EDX. Synthesis of Copper oxide nanoparticles can induce apoptosis and suppress the proliferation of Heal cells [20].

Many conventional methods are used for the preparation of iron nanoparticles. These are as following:-

1. Top-down approach.
2. Bottom-up approach

The methods of preparation of nanoparticles using physical methods, thermal decomposition, sonochemical synthesis, vacuum sputting are included in top-down approach. Whereas methods like co-precipitations, hydrothermal, hydrolysis methods comes under bottom-up approach. Top-down approach have many limitations like low production rate, requirement of energy, pressure, high temperature and thus it is more expensive. $NaBH_4$ is used as a reducing agent for the production of nanoparticles by bottom-up approach for the synthesis of nanoparticles but it is toxic to our ecosystem. Also many harmful by-products are released to our ecosystem [21].

So green synthesis methods are used for the preparation of iron nanoparticles. Nanoparticles are prepared in this method by using plant extract, microorganisms (like fungi, algae and yeast), bacteria. These are cost effective and also eco-friendly. Therefore green synthesis is a preferred over conventional method [22].

For the production of iron nanoparticles many researches are carrying out by using plants as they are cost effective as well as more eco-friendly. Iron nanoparticles are prepared by using green tea leaf extract, extract of terminalia chebula fruit, oolong and black tea leaf extract, banana peel extract [23].

Zero valent nanoparticles are prepared by using plants like Rosa damascene, Urtica dioica, Thymus vulgaris. Polyphenols, organic acids and proteins which are present in plant acts not only as a reducing agent but also stabilize the nanoparticles and prevent the aggregation of nanoparticles [24].

Many environmental issues are increasing day by day due to the increase in industrialization, excessive use of fertilizers in agriculture field which is a serious concern. So to remove these impurities from water nanoparticles are used. [26,27].

Scope of work

The concept of nanotechnology is very new to India and might take some time to get used to this technology. However people have realized the potential of this field in commercial field. It is also getting used in fields like electronics, healthcare markets, and other industrial products. Research and Development is going on to understand the growth of it in the market. The industry is growing in various sectors such as pharmaceuticals and medical products, electronics and computing, energy generation, textiles, metals, auto and auto components, aviation etc. Green synthesis is also used for the synthesis of nanoparticles which is eco-friendly and of low cost. Green synthesis of nanoparticles and their applications in sensing area is of great interest to the research community.

We prepare the nanoparticles of iron because it is present in haemoglobin. Iron helps to carry oxygen in our blood from lungs to tissues. Therefore it is most essential element for our body. Iron nanoparticles will be used in a drugs or in food materials so as to reduce the deficiency of iron in our body.

Experimental work:-

Three plants were chosen for the green synthesis of nanoparticles of iron.

1. **Neem plant:- It has so many medicinal use such as Anthelmintic, antifungal, antidiabetic, antibacterial, antiviral, contraceptive, and sedative. It is also used for skin diseases.**
2. **Tulsi plant: - It also have many uses like digestion aid, stress relieve, immune support, for the treatment of fever etc.**
3. **Pudina (metha):- It is used for headaches, rhinitis, cough sore throat, colic, and prurigo and vomiting.**

Process for the preparation of plant extract:-

1. **Tulsi - water extract :-**

   We took 10 g of the dried tulsi leaves along with bushes and 300 ml of distilled water is added into it. Boiled it for 3 hours and filter the extract. Extract is stored in refrigerator.

2. **Neem - water extract:-**

   We Took 10 g of the dried neem leaves along with the bushes and 300 ml of distilled water is added into it. Boiled it for 3 hours and filter the extract. Extract is stored in refrigerator.

3. **Pudina - water extract:-**

   We took 10 g of the dried Pudina leaves and bushes. 300 ml of distilled water is added into it. Boiled it for 3 hours and then filter the extract. Extract is stored in refrigerator.

4. Tulsi - ethanol extract:-

For the preparation of tulsi and ethanol extract we used soxhlet apparatus. We took 10 g of the dried leaves and bushes of tulsi in the thimble and 200 ml of ethanol in the round bottom flask. The condenser is fitted and place it on heating plate. Allow this process for 3-4 hours. Then we collected the extract prepared in round bottom flask. Extract is stored in refrigerator.

5. Neem - ethanol extract:-

For the preparation of neem and ethanol extract we used soxhlet apparatus. We took 10 g of the dried leaves and bushes of tulsi in the thimble and 200 ml of ethanol in the round bottom flask. The condenser is fitted and place it on heating plate. Allow this process for 3-4 hours. Then collect the extract prepared in round bottom flask. Extract is stored in refrigerator.

6. Pudina - ethanol extract:-

For the preparation of Pudina and ethanol extract we used soxhlet apparatus. We took 10g of the dried leaves and bushes of tulsi in the thimble and 200 ml of ethanol in the round bottom flask. The condenser is fitted and place it on heating plate. Allow this process for 3-4 hours. Then collect the extract prepared in round bottom flask. Prepared extract is stored in refrigerator.

Preparation of nanoparticle:-

Method 1:-

Prepared 10% solution of $FeCl_3$. Mixed the extract and $FeCl_3$ solution in the ratio of 2:1.

Result:-

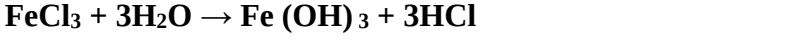
- Nano particles were observed in the case when we mix the $FeCl_3$ solution with extract of tulsi, Pudina, neem which is prepared in ethanol using soxhlet apparatus.
- No any nanoparticle was observed when the $FeCl_3$ solution mixed with extract of tulsi, neem, Pudina which is prepared by water.
- But we were not able to isolate the nanoparticles. We also used centrifuge technique to isolate the nanoparticles. But we were not able to isolate the nanoparticles.

Method 2:-

1. Preparation of ferric hydroxide:-
    - We took 5g of ferric chloride and dissolved it in 20 ml of water. Prepared 30% w/v solution of sodium carbonate.
    - Sodium carbonate solution is added to the ferric chloride solution dropwise till the pH reaches to 2.2. pH metre was used to monitor the pH. Then the mixture was allowed to stand at room temperature for 20 min.
    - After that addition of sodium carbonate is continued till the pH reaches to 4. At this pH we allowed the mixture to stand at room temperature for 30 minutes so that the precipitates will settle down.

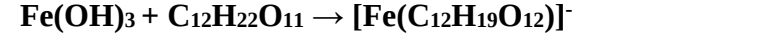
- Filtered the mixture and washed the precipitates of ferric hydroxide with 25 ml distilled water.
- Prepared a slurry of precipitates and water (20 ml).

Scheme 1. Preparation of ferric hydroxide.



2. Preparation of iron sucrose complex:-
    - We took three necked round bottom flask fitted with reflux condenser and a stirrer assembly.
    - 15 ml water and 30 g sucrose was added to the round bottom flask. Then the mixture was heated in the oil bath and temperature is maintained around 120° C.
    - When the temperature of the mixture reached to 100-105^{o} C. 2ml of 20% w/v sodium hydroxide solution is added to it.
    - Then the slurry prepared in first step is added to the sucrose mixture over about 15 minutes. A clear solution of brown color was formed after the addition of ferric hydroxide is completed.
    - The reaction temperature was maintained around 100-150^{o} C for 2 hours.
    - The mixture is cooled at room temperature.

Scheme 2. Preparation of iron sucrose complex



3. Isolation of iron sucrose complex:-

- 300 ml of ethanol is added to the reaction mixture prepared in step 1 at 25^{o} C with stirring.
- A dark brown precipitates were collected by filtration.
- For the purification of the precipitates 10 ml of water is added and subsequently adding ethanol 50 ml to the dissolved product to precipitate a purified product.
- Precipitates were filtered and washed with ethanol and dried under vacuum at 50^{0} C.

After the preparation of this iron sucrose complex. We took 1 g of the iron sucrose complex in a centrifuge tube and make the volume up to 5 ml by adding plant extract which is prepared by water and ethanol. Centrifuge is done for 4 hours.

Result:-

- Iron sucrose complex was insoluble in plants extracts which was prepared by ethanol.
- Iron sucrose complex was soluble in plant extract prepared by water as a solvent.

- A brown precipitates were observed in the case of plant extract prepared by water.
- No any precipitate was found in case of plant extract prepared by ethanol.

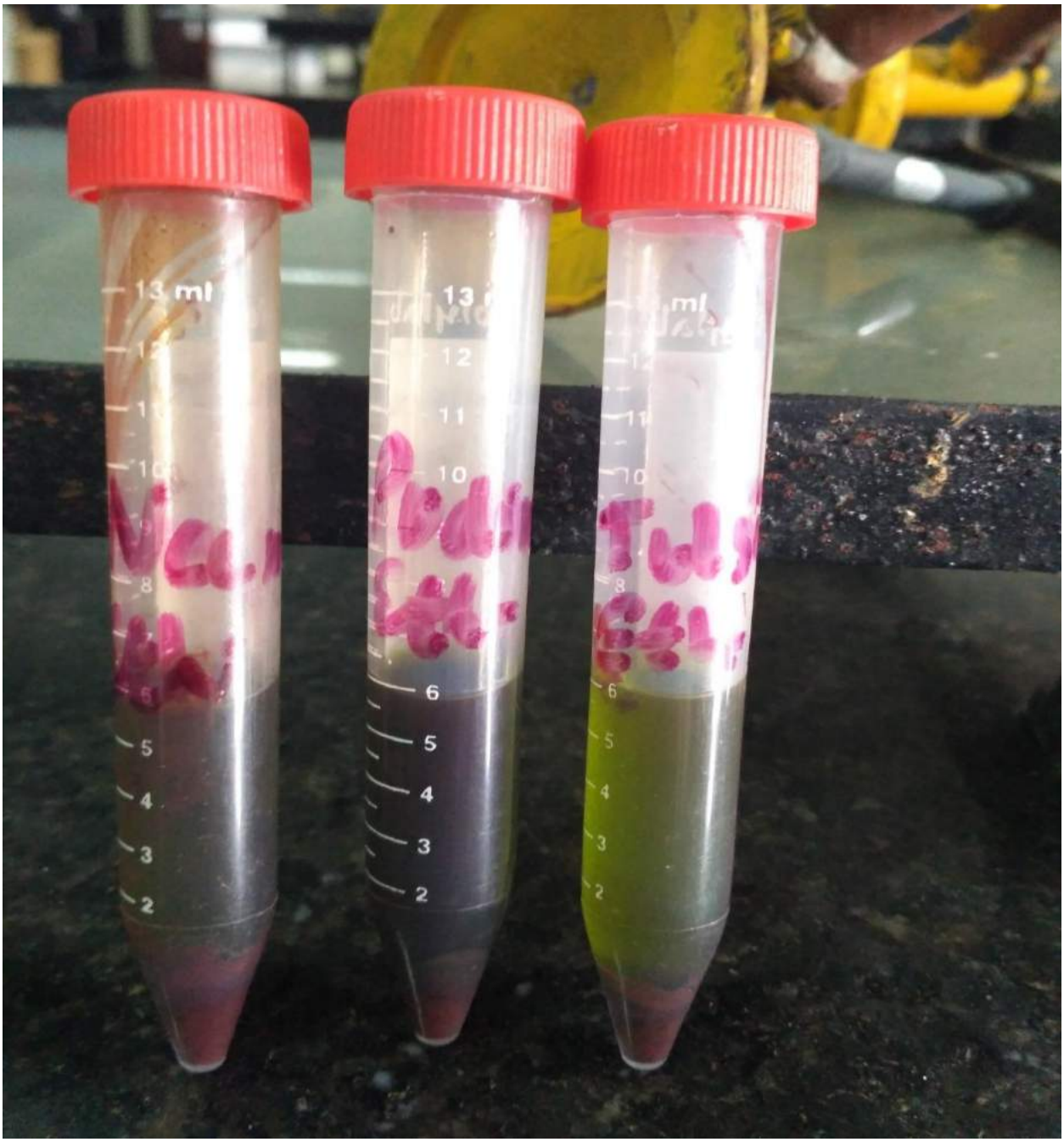


Fig 1. Iron sucrose complex was not soluble in either of the extract prepared in ethanol.

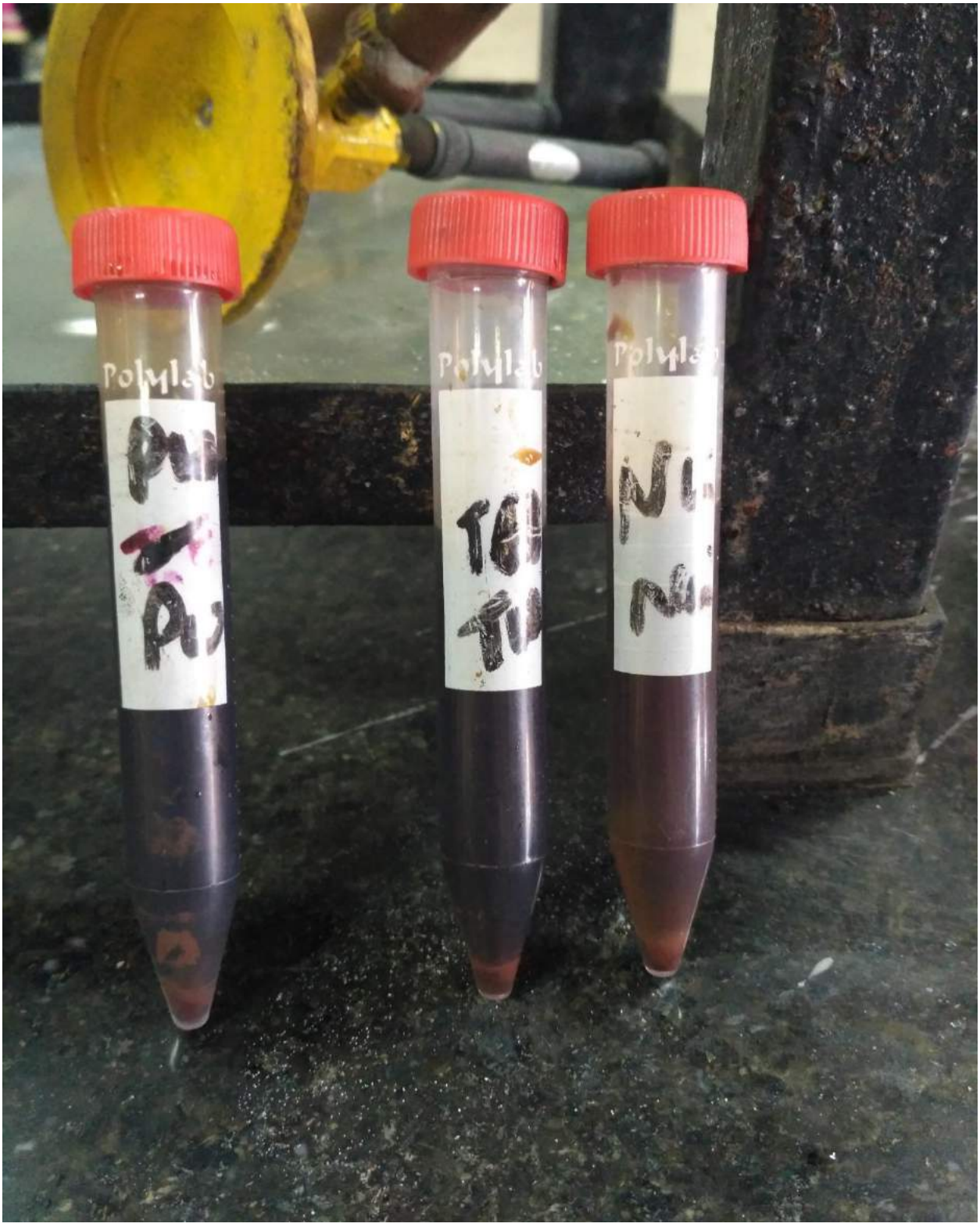


Fig 2. Precipitates were formed when iron sucrose complex was centrifuged with pudina and water extract, tulsi and water extract, neem and water extract (from left to right).

Method 3:-

- 0.25 g of $FeCl_3$ was taken in six centrifuge tubes.
- 5 ml plant extract (neem water, tulsi water, pudina water extract, neem ethanol, tulsi ethanol, pudina ethanol) was added in each of the centrifuge tube.
- The centrifuge tubes were allow to stand for 24 hours.
- Then it was centrifuge for 5 hours.

Result:-

Precipitates were observed in 3 centrifuge tubes which contain $FeCl_3$ with neem and water extract, tulsi and water extract, pudina and water extract. No any precipitate was appear in ethanol containing extract.

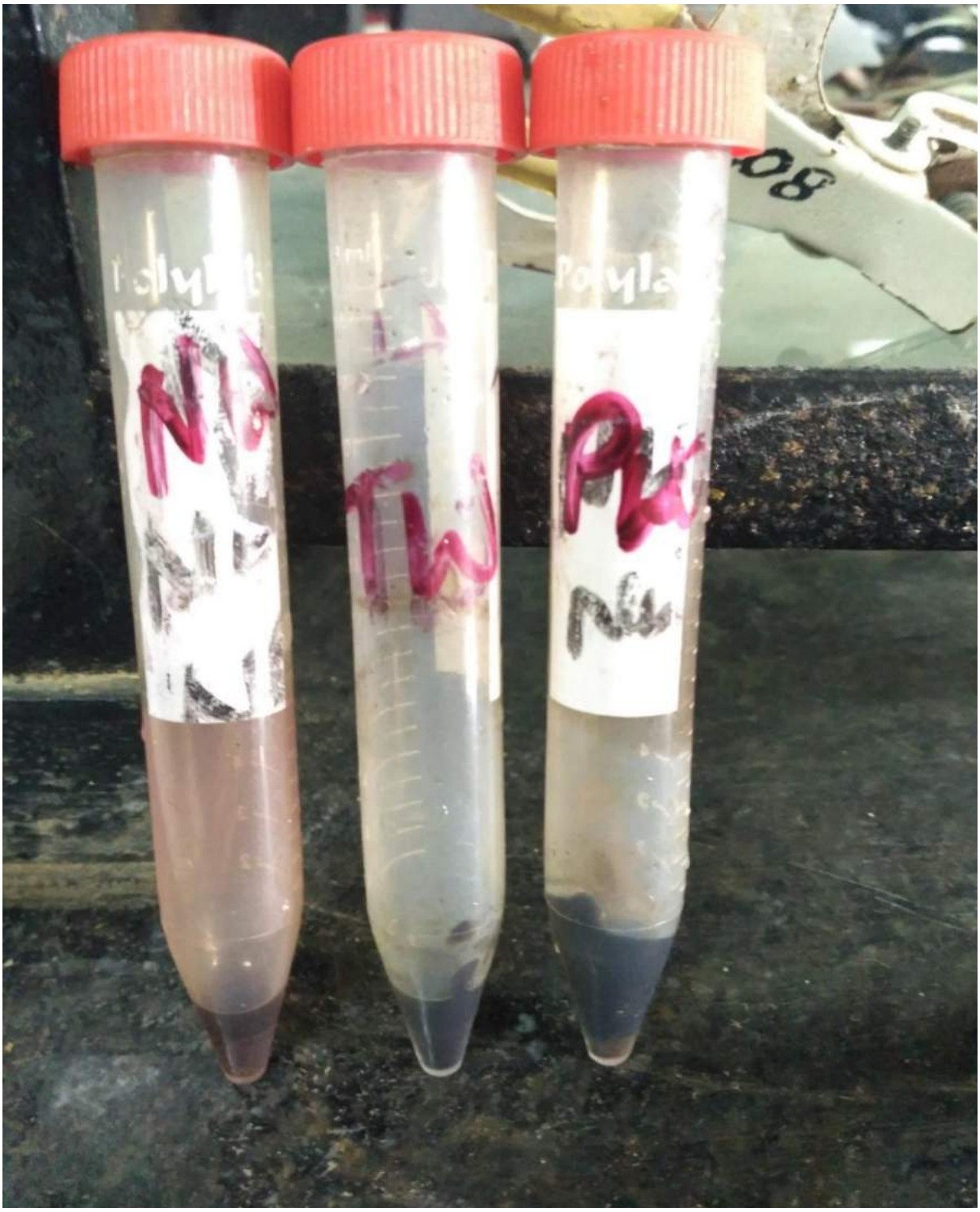
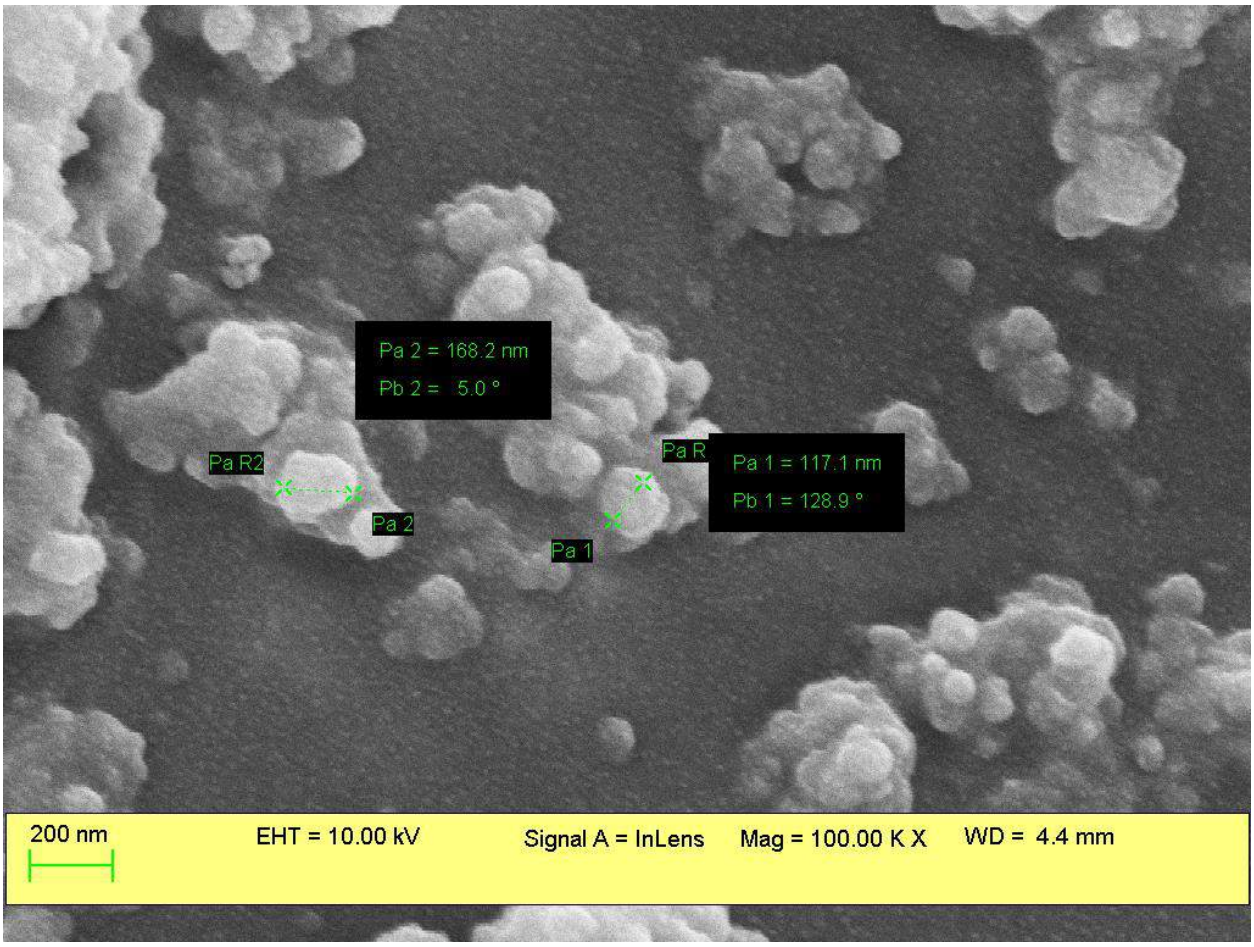


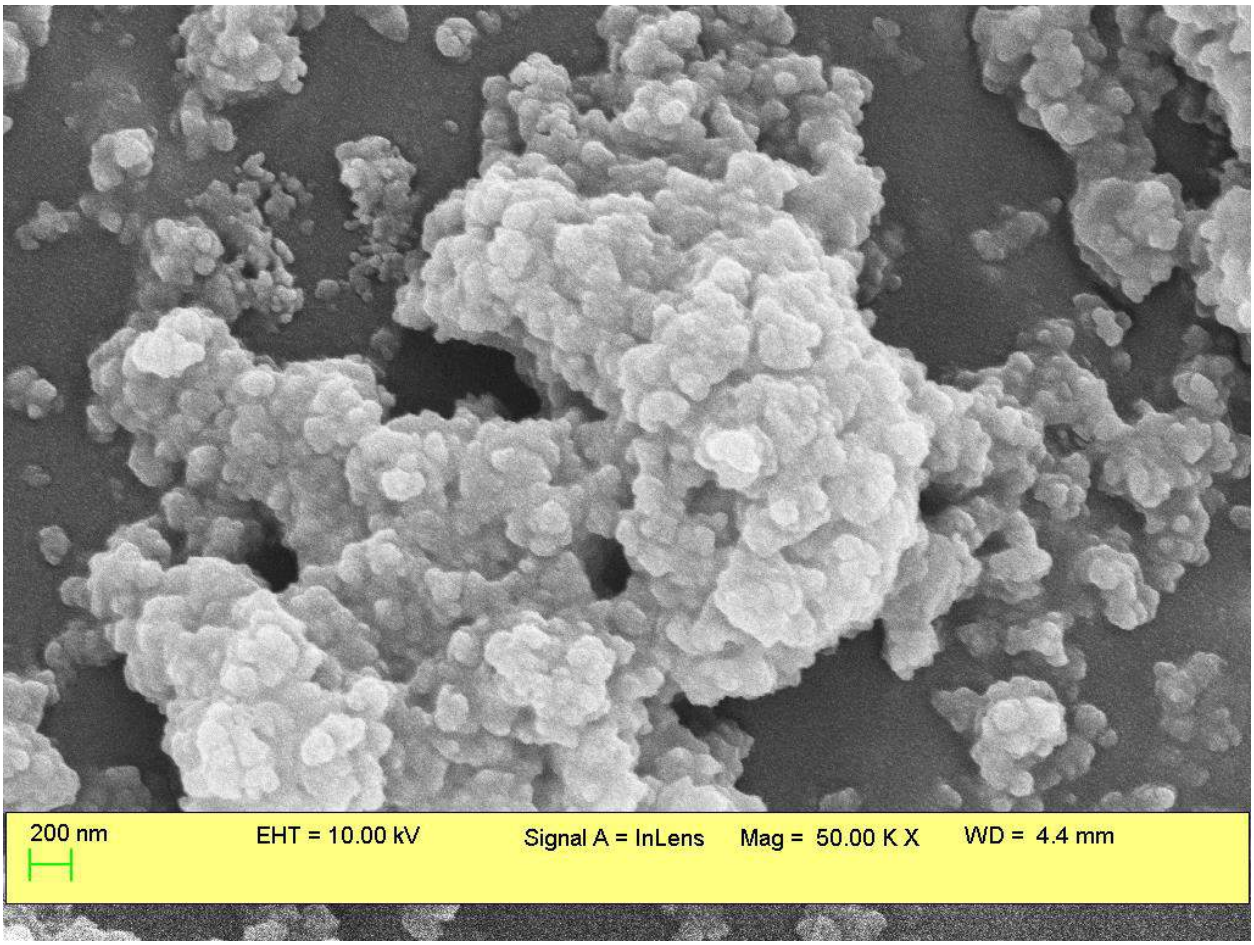
Fig 3. Precipitates were formed with neem water extract, tulsi water extract, pudina water extract.(left to right).

RESULT AND DISCUSSION:-

The analysis of nanoparticles formed is done by using SEM (scanning electron microscope). This technique is used to identify the size and structure of the particles. The electrons beam scan the surface of the particles and we get the images of those samples.

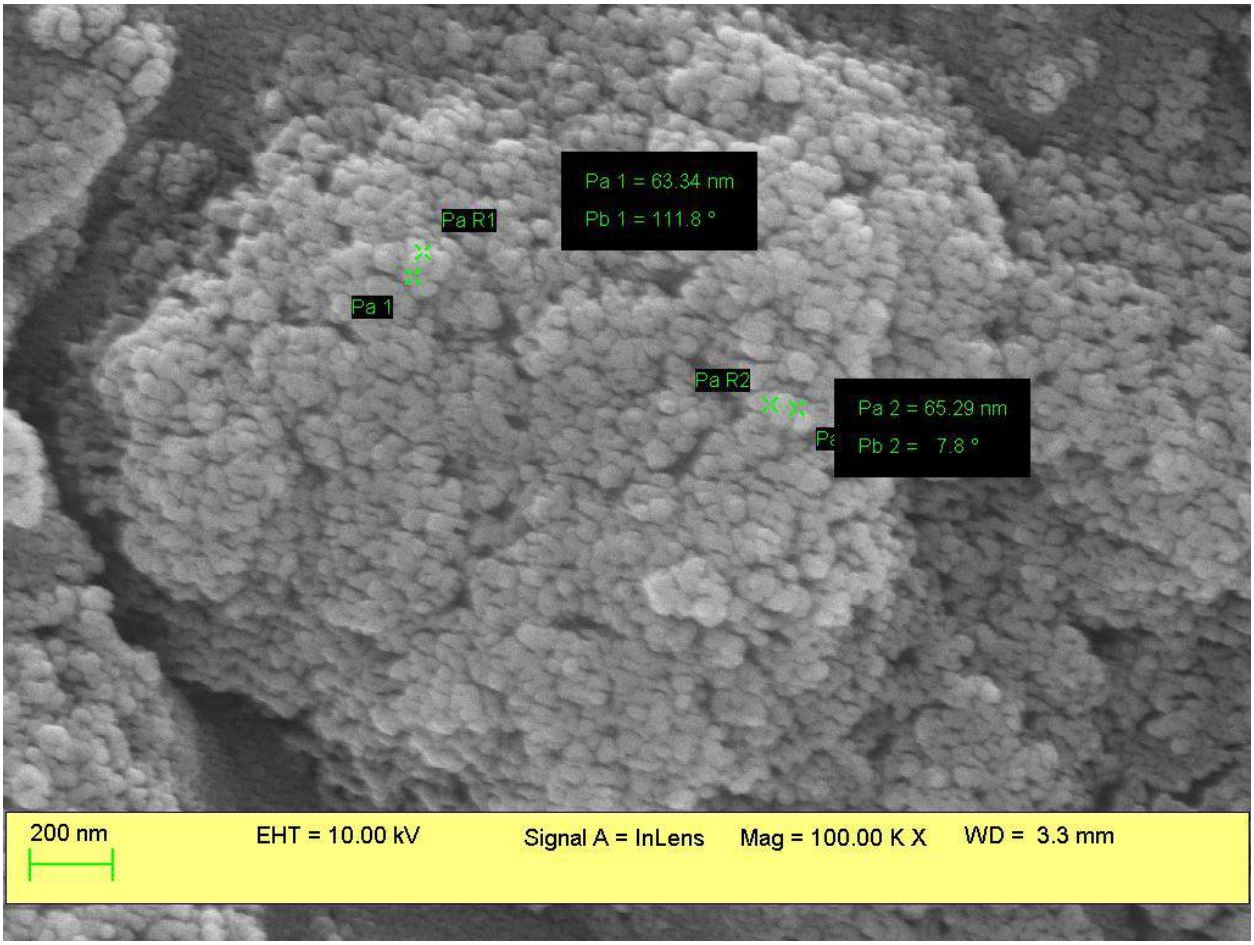
SEM image 1:- Nanoparticles of iron prepared by neem - water extract.

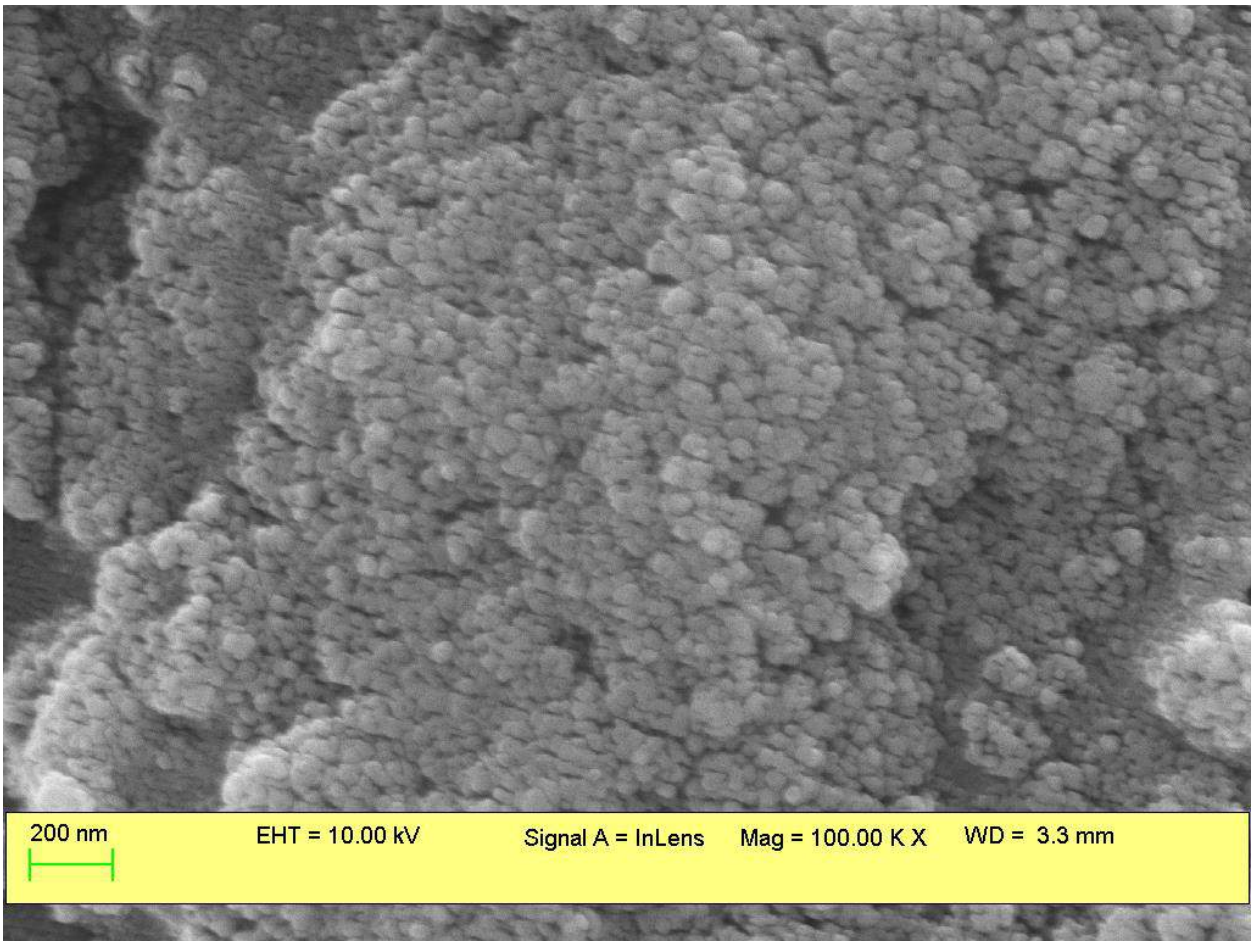




SEM images of the nanoparticles of iron prepared by using neem and water extract in $FeCl_3$. The particles size observed in this case was 168.2 nm and 117.1 nm.

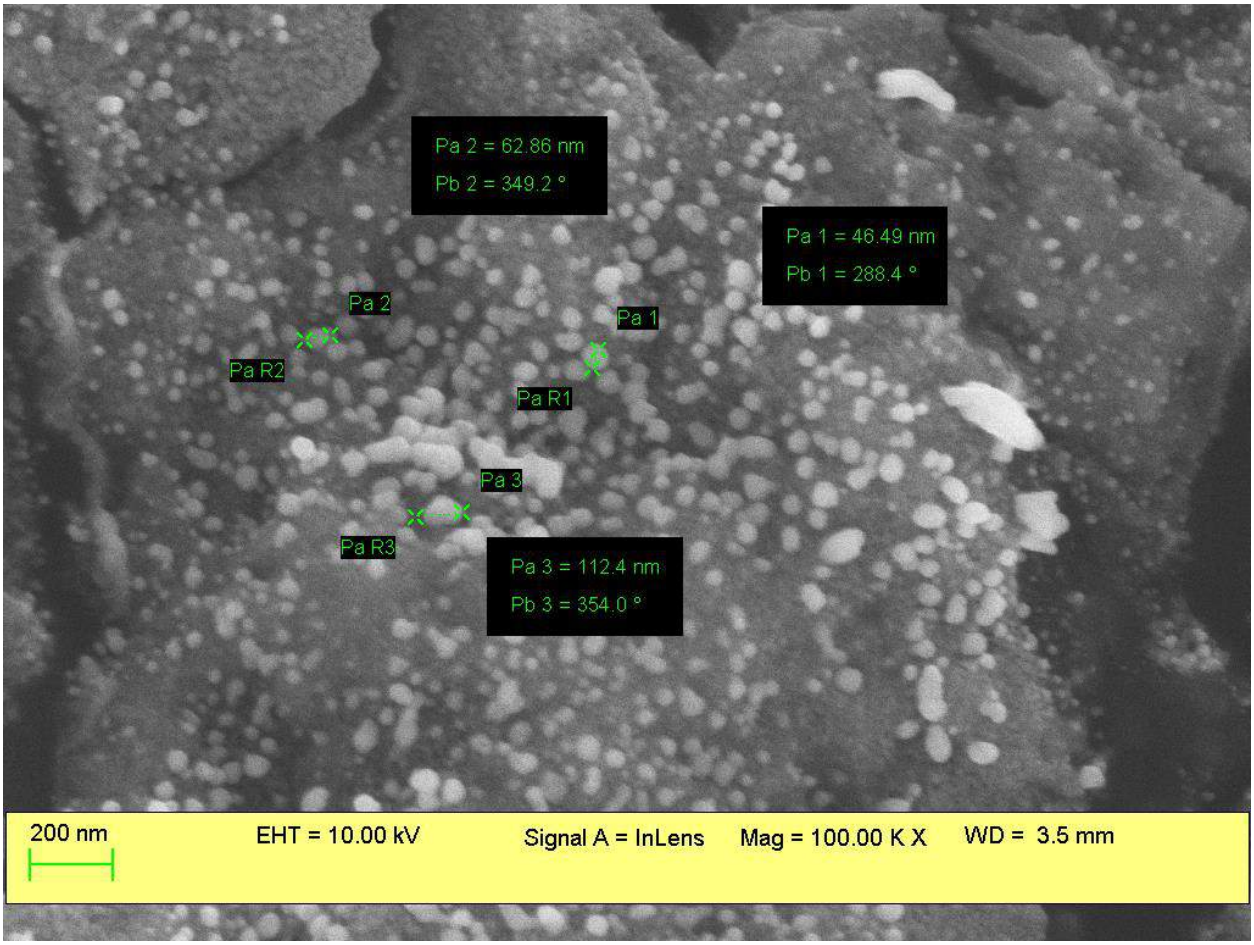
SEM image 2:- Nanoparticles of iron prepared by neem - water extract.

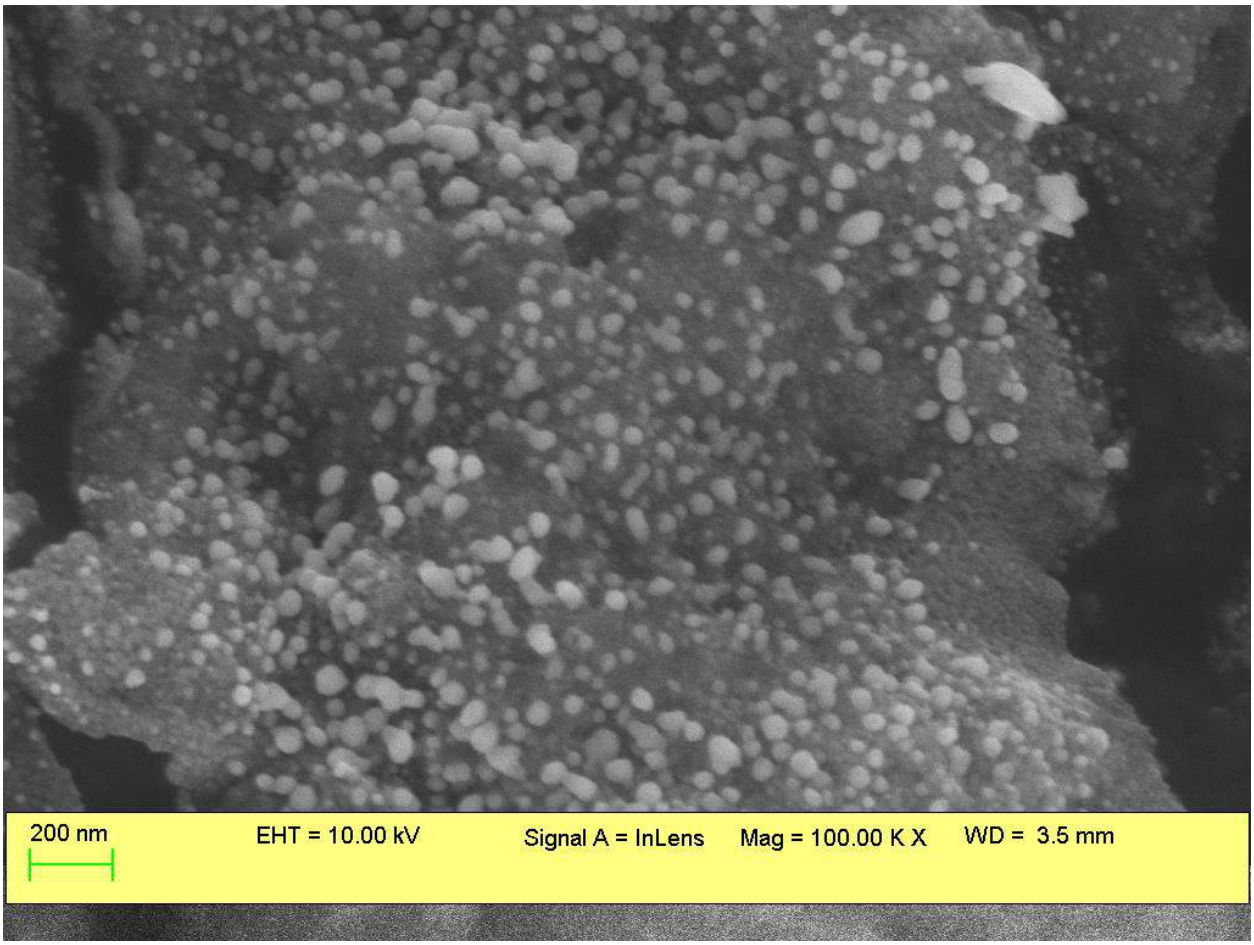




SEM images of the nanoparticles of iron prepared by using pudina and water extract in $FeCl_3$. The particles size observed in this case was 63.34 nm and 65.29 nm.

SEM image 3:- Nanoparticles prepared by using tulsi - water extract.





SEM images of nanoparticles of iron prepared by using Tulsi and water extract in $FeCl_3$. The particle size observed in this case was 46.49 nm and 62.86 nm.

Following is the table of the result observed:-

Extract	NP observed	Size
Neem + water – $FeCl_3$	Yes	117.1 nm
Pudina + water- $FeCl_3$	Yes	63.34 nm
Tulsi + water – $FeCl_3$	Yes	46.49 nm
Neem + ethanol- $FeCl_3$	No	-
Pudina + ethanol- $FeCl_3$	No	-
Tulsi + ethanol- $FeCl_3$	No	-
Iron sucrose with neem water extract	yes	Result awaited
Iron sucrose with tulsi water extract	Yes	Result awaited
Iron sucrose with pudina water extract	Yes	Result awaited

CONCLUSION:-

The nanoparticles are formed by using plants extract which are prepared in water. The analysis of those nanoparticles are done by using SEM. Nanoparticles which are prepared from different plants extract have different size. The size of particle in case of neem and water extract is 117.1 nm, the size of particle in case of pudina and water is 63.34 nm and the size of particle in case of tulsi and water is 46.49 nm. Therefore the best result is in the case of tulsi and water extract as the particle size in this case is smallest among all.

References

1. Harekrishna Bar, D.K.B., Gobinda sahoo P, priyanka Sarkar, Sankar PD., "Green synthesis of silver nanoparticles using latex of Jatropha curcas.". Colliod surface A, 2009. **39(3)**: p. 134-139
2. Cassandra D, N.N., Jodi H, Linfeng G, Tan, Li, et al, "Green synthesis of gold and silver nanoparticles from plant extracts." P.
3. DeSimone, J. M. Practical approaches to green solvents.Science 297 (2002): pp.799–803
4. Raveendran,P., Fu,J.,Wallen, S.L. Completely green synthesis and stabilization of metal nanoparticles. Journal ofthe American Chemical Society 125 (2003): pp. 13940–13941
5. Garima Singhal , R.B., Kunal Kasariya , Ashish Ranjan Sharma , Rajendra Pal Singh, "Biosynthesis of silver nanoparticles using Ocimum sanctum (Tulsi) leaf Page | 57 extract and screening its antimicrobial activity.". J Nanopart Res, 2011. 13: p. 2981-2988.
6. Spring H, S.K., "Diversity of magnetotactic bacteria.". Syst Appl Microbiol, 1995.
    a. 18(2): p. 147-153.
7. Sastry M, A.A., Islam NI, Kumar R., *"Biosynthesis of metal nanoparticles using fungi and actinomycetes."*. Current Sc., 2003. **85(2)**: p. 162-170.
8. Sastry M, A.A., Khan MI, Kumar R., *"Microbial nanoparticle production in Nanobiotechnology."*. Nanobiotechnology, 2003. **85(2)**: p. 163-169.

9. Elumalai EK, P.T., Hemachandran J, Vivivan Therasa S, Thirumalai T, David E., *"Extracellular synthesis of silver nanoparticles using leaves of Euphorbia hirta and their antibacterial activities."*. J Phram Sci, 2010. **2(9)**: p. 549-554.
10. Feynman, R. (1959) Lecture at the California Institute of Technology, December 29
11. Huang, J., Chen, C., He, N., Hong, J., Lu, Y., Qingbiao, L., Shao, W., Sun, D.,Wang, X H.,Wang, Y., Yiang, X. Biosynthesis of silver and gold nanoparticles by novel sundriedCinnamomum cam- phora leaf. Nanotechnology 18 (2007):pp.105–106
12. Sobha, K., Surendranath, K., and Meena, V. Emerging trends in nanobiotechnology. Biotechnology and Molecular Biology Reviews5(2010):pp. 001-012
13. Chan, H., Tsai, M. H. Synthesis and characterization of ZnO nanoparticles having prism shape by a novel gas condensation process. Reviews on Advanced Material Science 18 (2008): pp. 734- 743
14. Rai, M.,Yadav, A.,Gade, A.Current trends in photosynthesis of metal nanoparticles. Critical Reviews in Biotechnology 28(4)(2008):pp.277-284
15. Oliveira, M.U., D.; Zanchet, D. & Zarbin, A., "Influence of synthetic parameters on the size, structure, and stability of dodecanethiol-stabilized silver nanoparticles". J Colloid Interface Sci, 2005. **292**: p. 429-435.
16. Ankamwar, B.D., C.; Ahmad, A. & Sastry, M., "Biosynthesis of gold and silver nanoparticles using Emblica officinalis fruit extract, their phase transfer and transmetallation in an organic solution". J Nanosci Nanotechnol, 2005. **5**: p. 1665-1671.
17. Jha, A., Prasad, K, Prasad, K, Kulkarni, AR, *"Plant system: nature's nanofactory"*. Colloids Surf. B Biointerfaces, 2009. **73**: p. 219-223.

18. Sangeetha, G., Rajeshwari, S., Venckatesh, R. Green synthesis of zinc oxide nanoparticles by aloe barbadensis miller leaf extract: Structure and optical properties, Materials Research Bulletin 46 (2011): pp. 2560–2566
19. Gunalan, S., Sivaraj, R., Rajendran, V. Green synthesized ZnO nanoparticles againstbacterial and fungal pathogens.Progress in Natural Science: Materials International10 (2013): pp. 1002- 1016
20. Kasthuri J, K.K., Rajendran N., *"Phyllanthin assisted biosynthesis of silver and gold nanoarticles a novel biological approach."*. J Nanopart Res, 2009. **11**: p. 1075-1085.
21. Guidelli EJ, R.M., Zaniquelli D, Baffa O., *"Green synthesis of colloidal silver nanoparticles using natural rubber latex extracted from Hevea brasiliensis."*. Mol Biomol Spectrosc, 2011. **82(1)**: p. 140-145.
22. T. Shahwan, S. Abu Sirriah, M. Nairat, E. Boyacı, A.E. Erog˘lu, T.B. Scott, K.R. 548 Hallam, Green synthesis of iron nanoparticles and their application as a 549 Fenton-like catalyst for the degradation of aqueous cationic and anionic dyes, 550 Chem. Eng. J. 172 (2011) 258–266.
23. L. Huang, X. Weng, Z. Chen, M. Megharaj, R. Naidu, Synthesis of iron-basednanoparticles using oolong tea extract for the degradation of malachite green, Spectrochim. Acta Part A Mol. Biomol. Spectrosc. 117 (2014) 801– 570 804.
24. V. Madhavi, T.N.V.K.V. Prasad, A.V.B. Reddy, B. Ravindra Reddy, G. Madhavi, Application of phytogenic zerovalent iron nanoparticles in the adsorption of hexavalent chromium, Spectrochim. Acta Part A Mol. Biomol. Spectrosc. 116 (2013) 17–25.

25. H. Abdoallahzadeh, B. Alizadeh, R. Khosravi, M. Fazlzadeh, Efficiency of EDTA Modified nanoclay in removal of humic acid from aquatic solutions, J. Mazandaran Univ. Med. sci. 26 (2016) 111-125.

26. R. Khosravi, M. Fazlzadehdavil, B. Barikbin, H. Hossini, Electro-decolorization of Reactive Red 198 from aqueous solutions using aluminum electrodes systems: modeling and optimization of operating parameters, Desalin. Water Treat. 54 (2015) 9.