**Urtica Dioica** Leaves Extract: A Natural Resource to Reduce Iron Salt to Synthesize Fe Nanoparticles

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**Abstract:** This paper demonstrates synthesis of iron nanoparticles by using leaves extract of *Urtica Dioica* plant, a natural resource to reduce the iron salt. Moreover, leaves extract also acts as a stabilizing agent in protecting dispersed Fe nanoparticles. The absorption peak is observed in the range of 367-427 nm, indicating formation of Fe nanoparticles, however with partial oxidation. The Fe nanoparticles were obtained in powder form after centrifugation, thorough washing and drying processes. Fe nanoparticles were further analyzed by different analytical techniques like; XRD, SEM, TEM and XPS. The size range of the synthesized Fe nanoparticles was found to be dependent on leaves extract concentration which further influences structure and hence stability. Signature of oxidation also was revealed by XPS studies after long exposure to air ambient.

1. **Introduction**

In recent years, iron nanoparticles have displayed many efficient activities in the areas of biomedicine [1][1], sensors [2], batteries [3] and clean up technologies [4, 5]. Numerous chemical and physical methods for producing these nanoparticles have been reported [6, 7]. However, level of purity and toxicity due to use of chemicals are key issues involved in the production of nanoparticles. [8]. Thus, green methodology offers eco-friendly alternative to overcome the drawback to some extent. “Green methodology” can be normally categorized as a process, which consumes less energy and used natural resources as chemicals to perform reactions. [9] Plants, one of the natural resources, contain flavonoids, flavones, isoflavones, isothiocyanates, carotenoids, polyphenols etc, which can reduce metal salts [10]. Different plants parts in the form of extract have been used to synthesize different metal nanoparticles. Iron nanoparticles have also been synthesized by using different plants like green tea [11], Terminalia chebula [12], *Eucalyptus tereticornis*, *Melaleuca nesophila* and *Rosemarinus officinalis* [13], *Azadirachta indica* [14] and *Grapes* [15]. However, in most of these studies, almost complete oxidation of synthesizing iron nanoparticles has been reported. Very recently synthesis of the iron nanoparticles by using *Urtica dioica* leaves has been reported but the nanoparticles were observed in amorphous form [16]. In our study, we are reporting the synthesis of crystalline iron nanoparticles by using the leaves extract of *Urtica dioica* without adding any external capping agent.

2. **Material and Methodology**

*Urtica Dioica* Leaves were collected from the local region of Srinagar (Garhwal) Uttarakhand, India. The collected leaves were thoroughly washed with double distilled water then air dried and afterwards crushed. Three different extract concentrations was prepared with 100 ml of double distilled water by mixing 10
gm, 5 gm and 2.5 gm of crushed leaves and heating the mixtures at 40° C for 30 minutes. FeCl₃ (Fisher’s Scientific 99.99 %) 0.1 M salt solution was used as a reduction solution and was mixed with leaves extract with 2:1 volume ratio. Change in color from light green to black was noticed at all extract concentrations and normally taken as an indication of reduction of FeCl₃ into iron species and finally formation of Fe nanoparticles. After some time, settling of iron nanoparticles was seen at the bottom of flask. The reduction time and settling of synthesized Fe nanoparticles were found to be dependent on extract concentration. The Fe nanoparticles were collected after centrifugation at 3000 rpm for 5 minutes, followed by the thorough washing using double distilled water and then moderate drying. Effect of extract concentration on reduction time and on the yield of synthesized Fe nanoparticles is shown in figure 1. As clear from the figure 1, as the extraction concentration increases reduction time reduces whereas yield increases. This trend seems to be obvious, larger extract concentration means presence of more reducing species leading to more and faster reduction of FeCl₃ into iron species, thereby production of more Fe nanoparticles.

UV-VIS spectral analysis was done by using Perkin Elmer’s Lambda 35 spectrophotometer. The synthesized nanoparticles were characterized by X’ Pert PRO PANalytical X-Ray Diffractometer. Surface morphology and elemental analysis was carried out by scanning electron microscopy (SEM, Zeiss, EVO 18 special edition). Transmission Electron Microscope (TEM, JEM-1400) was used for morphological study of the synthesized iron nanoparticles. X-ray Photoelectron spectroscopic (XPS) study was carried out by using Physical Electronics’ PHI 5000 Versaprobe III model to investigate composition and valence state of prepared iron nanoparticles.

3. Result and Discussion

Fe nanoparticle samples prepared with extract concentrations of 10 gm/100ml, 5 gm/100ml and 2.5 gm/100 ml, while keeping molarity of FeCl₃ salt solution 0.1 M, are mentioned as samples 1, 2 and 3, respectively. Absorption of Fe nanoparticles dispersed in distilled water, as measured by the UV-VIS spectrophotometer, are shown in figure 2. Two Absorption peaks are observed in each sample. In the

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Figure 1. Effect of leaves extract concentration on salt reduction time and yield of synthesized Fe nanoparticles.
sample 1, absorption peaks are observed at 369 and 418 nm. Similarly, in the sample 2, absorption peaks are seen at 369 and 410 nm. In the sample 3, absorption peaks are observed at 364 and 400 nm. The absorption peaks corresponding to the iron nanoparticles have been reported in the range 200-450 nm [16, 17] depending upon solvent and synthesis process.

![UV-VIS spectra of Fe nanoparticles corresponding to the samples 1, 2 and 3.](image1)

**Figure 2.** UV-VIS spectra of Fe nanoparticles corresponding to the samples 1, 2 and 3.

![X-ray diffraction patterns of the iron nanoparticles corresponding to the (a) sample 1 and (b) sample 2](image2)

**Figure 3.** X-ray diffraction patterns of the iron nanoparticles corresponding to the (a) sample 1 and (b) sample 2.
X-Ray diffraction pattern of synthesized Fe nanoparticles samples 1 and 2 are shown in the figure 3(a) and 3(b), respectively, clearly confirms the crystallinity of the prepared samples. However, in previous reports formation of amorphous iron nanoparticles has been reported by using the leaves of *Urtica dioica*. [16] It is important to mention here that x-ray diffraction of sample 3 could not be recorded due to high hydroscopic nature. In the x-ray diffraction pattern of sample 1, the peak positions (hkl) of Fe were observed at 2θ values of 21.40(004), 43.52(008), 49.63(200), 55.64(321) and 63.19(102) (JCPDS card no. 0111262, 894185 and 501275) indicating hexagonal structure, with additional minor peaks at 32.7 (111), 36.76 (018), 54.24 (215), 58.22 (127), 68.35 (223), indicating oxidation of Fe nanoparticles. Figure 3(b) shows the diffraction pattern of the sample 2 with peak positions at the 2θ (hkl) values of 28.24 (200), 55.24 (321), 46.85 (127), 77.07 (110) (jcpds card number 655099), with the additional peaks observed at 2θ (hkl) values of 32.64 (111) and 67.95 (222) which indicates the oxidation of iron nanoparticles in the sample 2. The x-ray diffraction pattern of the sample 2 contains peaks corresponding to both the cubic and hexagonal structures. The crystallite size of the synthesized iron nanoparticles was calculated using Debye’s Scherrer formula [16] and found between 13 - 25 nm for the sample 1 whereas 17 - 20 nm for the sample 2.

**Figure 4.** SEM images of iron nanoparticles (a) sample 1, (b) sample 2, (c) sample 3 and (d) EDX iron nanoparticles related to the sample 1.

Figure 4 (a, b, c) shows the SEM images of synthesized iron nanoparticles of the sample 1, 2 and 3, respectively. The micrographs clearly show that the synthesized nanoparticles are in the agglomerated state. Figure 4(d) shows the energy dispersive X-ray analysis (EDAX) of the synthesized iron nanoparticles corresponding to sample 1. The EDAX of iron nanoparticle sample 1 shows presence of iron along-with other elements like carbon, oxygen, calcium, Chlorine, potassium. The presence of additional elements has been arisen from the used plant extract as plants contain these elements.
Figure 5 shows the TEM images of the synthesized iron nanoparticles. In the TEM image, figure 5(a), of the sample 1 some edges, but not clear hexagonal symmetry can be seen in the agglomerated structure, as revealed by corresponding XRD pattern (figure 3a). The SEAD shown in the figure 5(a) inset also show very faded rings. This is due to the large concentration of plant extract residues, mostly in the form of amorphous carbon, present onto the particles, which is making very difficult to probe the particles with electron microscopy. Similarly, in the iron nanoparticles sample 2 (figure 5(b)), the shape of agglomerated nanoparticle is not very clearly displayed while imaging. Almost spherical iron nanoparticles connected through amorphous carbon like chain-structure are seen in the sample 3, as displayed in figure 5(c). Selected area diffraction pattern (SAED) corresponding to the sample shows distinct rings indicating crystalline cubic structure although it was not possible to obtain by x-ray diffraction. The diameter of the iron nanoparticles from the TEM images was estimated using Image-J software by considering surface area of the nanoparticles. In the samples 1, 2 and 3, the diameter of Fe nanoparticles were found in the range 68-238 nm, 53-94 nm and 16-35 nm, respectively. As mention before, the samples 1, 2 and 3 were prepared with extract concentration 10gm/100ml, 5 gm/100ml and 2.5 gm/100ml, respectively. The concentration of reducing agent determines the rate of reduction of salts and thus, produced primary species concentration which finally coagulates to produce nanoparticles. Coagulation rate and thus size of the produced nanoparticles, normally depends on the primary species concentration present in the solution. Therefore, as the extract concentration reduces the size of synthesized Fe nanoparticles get smaller and size-distribution becomes narrower. Thus, the extract concentration plays a key role in controlling size and size-distribution of synthesized nanoparticles.

![Figure 5. TEM images of iron nanoparticles (a) sample 1 (inset SAED pattern), (b) sample 2 and (c) sample 3(d) SEAD pattern corresponding to the sample 3.](image-url)
The greenly produced iron nanoparticles were further analyzed via XPS to study their oxidation state. Figure 6(a) shows the survey spectrum of the iron nanoparticle sample 1, which indicates the presence of Carbon 1s, Oxygen 1s, Iron 2p and Nitrogen 1s peaks [18]. The carbon 1s core level (figure 6(b)) was observed to consist of the peaks at the binding energies 283.36 eV, 284.14 eV, 285.0 eV and 287.5 eV attributed to C-H, C-C, C=C and C=O bonding state of carbon [19]. The existence of these bonding states of carbon indicates that the C-H, C-C, C=C and C=O groups present in the plant leaves extract are mainly responsible for reducing the salt and thus stabilizing the synthesized nanoparticles. Figure 6(c) shows the deconvolution of Fe 2p core level peak, which clearly indicates that Fe is in +2 and +3 oxidation states. The fitted peaks at the binding energies 710.35 eV and 724.36 eV were reported corresponding to 2p3/2 and 2p1/2 levels of Fe in +2 oxidation state, respectively. Similarly, fitted peaks at 714.0 eV and at 722.35 were found to resemble with 2p3/2 and 2p1/2 of Fe in +3 oxidation state [20]. It is necessary to mention that the XPS measurement was performed after months of synthesis and at different laboratory, therefore, has undergone long exposure to air ambient. Therefore, no trace of metallic Fe is realized in the spectra.

Figure 6. XPS (a) survey (b) C1s and (c) Fe2p spectra corresponding to the iron nanoparticles sample 1.

4. Conclusions
Iron nanoparticles were successfully synthesized via facile green route by using the leaves extract of Urtica Dioica plant without using any other external capping agent. The size and size-distribution were found to depend on the extract concentration. Relatively smaller size with narrower size-distribution is
observed in iron nanoparticles prepared with lesser leaves extract concentration. Fe nanoparticles prepared with 10gm/100ml extract solution revealed hexagonal structure. With leaves extract 5gm/100 ml mixed hexagonal and cubic structured Fe nanoparticles were obtained. On reducing the leaves extract concentration to 2.5 gm/100 ml cubic structured Fe nanoparticles was prepared, which shows hygroscopic in nature on air exposure. Presence of iron in +2 and +3 oxidation state in XPS study further confirmed the oxidation of the iron nanoparticles after long exposure to ambient.

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