



Effective Parameters in the Green Synthesis of Zero-valent Iron Nanoparticles as a Fenton-like Catalyst

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Abstract

Nowadays, utilization of new and sustainable techniques for the synthesis of INPs are increasing significantly. Common nettle (*Urtica dioica*) or stinging nettle is an herbaceous perennial flowering plant with a significant reduction potential. Leaf extract of this plant can reduce iron ions to zero-valent INPs. Like all chemical and biochemical reactions, reaction conditions have an immense effect on the process. In this experiment, impacts of different process parameters such as FeCl_3 concentration, leaf extract quantity, reaction temperature, and reaction time on the biosynthesis of INPs were evaluated. FeCl_3 concentration, quantity of the leaf extract, and reaction temperature were identified as effective factors. But, reaction time has not any significant impact. INPs were characterized by transmission electron microscope (TEM) Fourier transform infrared (FTIR) spectroscopy, and X-ray diffractometer. Particles were spherical and oval in shape and were measured to be 21–71 nm with mean particle size of 46 nm. TEM illustrated that the zero-valent iron (ZVI) nanoparticles had mostly a spherical shape with 46 nm of mean diameter. The particles tend to form irregular clusters with phytochemicals from leaf extract and form macrostructures in the range of 117–605 nm. Prepared nanostructures are a promising catalyst in Fenton reactions and can degrade Methyl orange dye with about 70 percent efficiency in 5 h.

Keywords: Bioreduction; Biosynthesis; Common nettle; Fe nanoparticles; Plant mediated synthesis; *Urtica dioica*

1 Introduction

Nanoparticles retained so much attention in various fields of sciences and technologies due to their unique physicochemical and biological properties (1, 2). Among all nanoparticles, metal nanoparticles are employed in a variety of fields such as environmental remediations, bioprocess intensification, bioseparation, pharmaceutical sciences, and nanomedicine (3). Among these nanoparticles, there has been special focus on iron nanoparticles (INPs) due to their unique properties such as ease of synthesis and functionalization, magnetic behavior, catalytic activity, and biocompatibility (4). These nanoparticles are now being applied in various fields including bioremediation (5),

biology and biotechnology (6, 7), ferrofluids (8), and medicine (9). Hence, production of INPs with various characteristics has attracted great attention (4, 10-12). Chemical synthesis is one of the primary techniques for synthesis of INPs. Since now chemical approaches have been developed significantly and are able to produce pure INPs with desirable characteristics. But, these techniques usually employ organic solvents and noxious chemicals and also are conducted at harsh conditions (13-17).

Biosynthesis has emerged as a potential sustainable alternative for chemical procedures (18-21). Biological compounds such as flavonoids, polyphenol, alkaloids, carbohydrates, proteins and other biomolecules can act as

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green bioreductant for synthesis of metal nanoparticles (22-27). These metabolites can also act as stabilizing agent to prevent agglomeration and improve dispersity and reactivity of nanoparticles (19, 21, 28, 29). Biosynthesis reactions have been conducted by using bioactive compounds from various organisms such as microbial cells, algae, and plants (19-21, 30). But, use of plant extracts for synthesis of INPs have considerable advantages over other organisms such as cheapness, availability, safety, less recovery steps and elimination of elaborate cell culture process (18, 31).

Recent studies have shown that INPs can be synthesized by using extracts of eucalyptus, *Castanea sativa*, some kinds of tea, mulberry, pomegranate, peach, pear, vine, coffee, *Salvia officinalis*, *Caricaya papaya*, tangerine, sorghum, and so many other plants (4). But, like all chemical and biochemical reactions, biosynthesis of INPs can be affected by reaction conditions (4, 30, 32). So, there is an increasing demand for investigations toward recovery of the effective factors in the biosynthesis of INPs.

Urtica dioica, also known as common nettle or stinging nettle, is an herbaceous perennial flowering plant in the family Urticaceae. *U. dioica* leaf extract contains various phytochemicals such as phenolic and flavonoid compounds, and has a long history of application in medicine and fooditarian (11, 33). In our previous study we have shown that leaf extract of this plant is so bioactive which can reduce ferric ion to zero-valent iron nanoparticles (11). In this study, the effect of different process parameters such as FeCl_3 concentration, leaf extract quantity, reaction temperature, and reaction time on the biosynthesis of INPs by using *Urtica dioica* leaf extract were evaluated.

2 Materials and methods

2.1 Materials

Ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, analytical grade), was purchased from Merck Chemicals (Darmstadt, Hessen, Germany) and used without any further treatment. Dried leaves of *U. dioica* were purchased from a local shop (Fasa, Fars, Iran). Millipore water (Millipore Corp., Bedford, MA, USA) was used throughout the whole experiment.

2.2 Leaf extract preparation

Dried leaves were washed to remove any impurities and were dried at room temperature. In order to prepare aqueous extract of nettle leaves, deionized water was added to the crushed leaves at a ratio of 1:20 (w/v) and boiled under reflux for 15 min by using a heater mantel (11). The prepared mixture was cooled to room temperature and filtered through a Whatman filter paper (Reeve angel, Grade 201). The filtrate was centrifuged for 5 min at 2000 rpm to eliminate plant microparticles. The obtained clear solution was stored in the refrigerator and was used as leaf extract.

2.3 Effective factors in the biosynthesis reaction

The effects of several parameters (i.e. FeCl_3 concentration, leaf extract quantity, reaction temperature, and reaction time) on the biosynthesis of INPs were evaluated by one factor at a time approach. After completion of each reaction, the prepared INPs were harvested by centrifugation and washed with deionized water. The resulting black pellets were oven-dried at 50°C for 48 h and

weighed to calculate the concentration of prepared nanoparticles.

2.4 Characterization of INPs

Visual appearance and morphological characteristics of INPs were investigated by Philips CM 10, TEM, operated at high voltage (HT) 100 kV. The INPs was diluted in millipore water and dried on a carbon-coated copper grid.

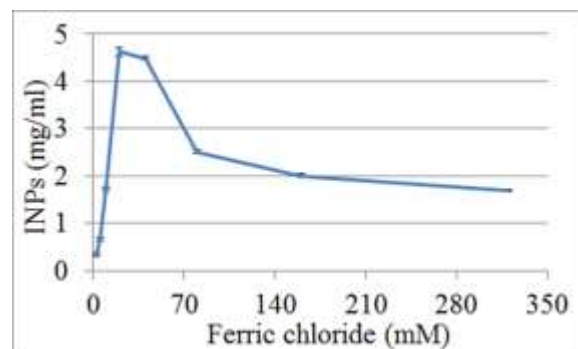


Figure 1: Effects of FeCl_3 concentration on the formation of INPs

Particles size distribution was obtained using Image J software version 1.47v, an image analysis software developed by the NIH. Main functionality of the INPs were evaluated by Fourier transform infrared (FTIR) spectroscopy using a Bruker, Vertex 70, FTIR spectrometer, and the standard KBr pellet method in the range between 400 cm^{-1} and 4000 cm^{-1} . Phase composition and crystallinity of INPs were obtained using Siemens D5000 x-ray powder diffractometer instrument. X-ray diffraction (XRD) pattern of INPs samples were scanned within the 2θ range from 20° to 90° and results were evaluated by PANalytical X'Pert HighScore software.

2.5 Fenton catalytic activity of INPs

Potential of the prepared nanostructures as a Fenton catalyst was evaluated in a dye degradation reaction. The experiment was performed at room condition in single-use 10 mL reaction volume (12). In brief, zero-valent iron nanoparticles (1 mg/mL final concentration in reaction) were mixed with Methyl orange dye solution (20 mg/L) containing one per cent H_2O_2 . The reaction was followed for 6 h and rate of dye degradation was calculated against methyl orange standard curve at 465 nm (Hitachi U-0080D UV-vis spectrophotometer, Tokyo Japan). A solution of Methyl orange and hydrogen peroxide without any nanostructure was set as the control.

3 Results and discussion

3.1 Effective factors in the biosynthesis reaction

The effects of iron precursor concentration on the biosynthesis of INPs were evaluated from 2.5 mM to 320 mM ferric chloride and results were shown in Figure 1. Increase in the concentration of iron precursor up to 20 mM resulted to increase in the amount of prepared INPs. But, interestingly, more increase in the iron precursor has shown negative effect on the formation of nanoparticles. Similar effects were also reported for the green synthesis of silver

nanoparticles (AgNPs). It is shown that high concentrations of silver precursor (AgNO_3) have an immense negative effect on the biosynthesis of AgNPs (25, 26).

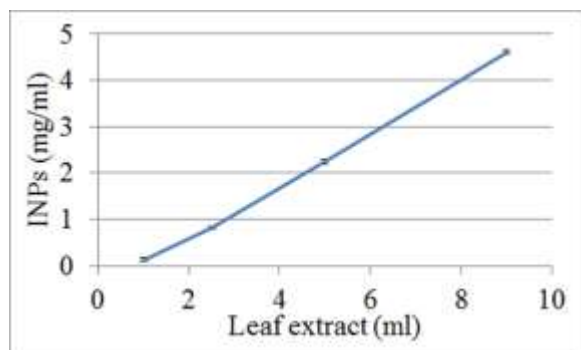


Figure 2: Effects of leaf extract quantity on the formation of INPs

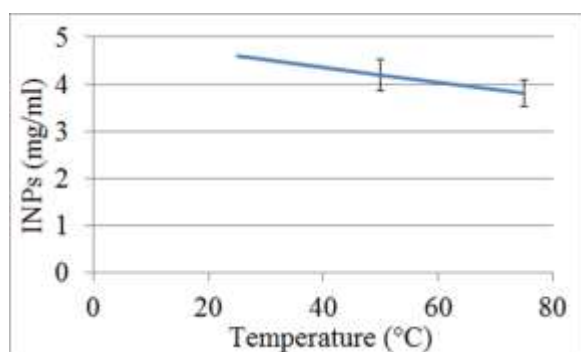


Figure 3: Effects of reaction temperature on the formation of INPs

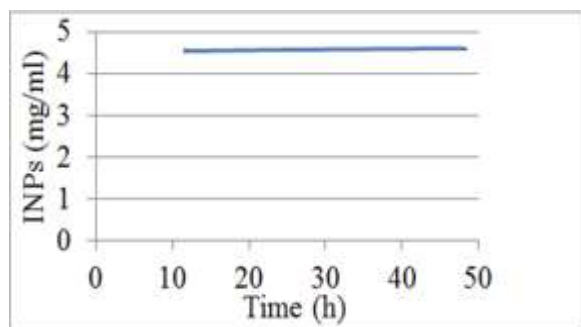


Figure 4: Effects of reaction times on the formation of INPs

The effect of *U. dioica* leaf extract quantity on the production of INPs is shown in Figure 2. The pattern revealed that amount of *U. dioica* leaf extract plays a significant role in the production of INPs and increase in the leaf extract quantity resulted in more nanoparticle production. Increase in the amount of leaf extract is equal to increase in the concentrations of bioactive compounds in the reaction and therefore more reduction of iron ions. The effect of reaction temperature was evaluated from 25°C to 75°C. Fortunately, room temperature (25°C) was identified as the best temperature for the bioreduction of iron ions (Figure 3). This means that bioreduction of iron ions by using *U. dioica* leaf extract is an economic reaction from energy consumption point of view which is so critical for scaling up

process and industrial production. Similar results were also reported for biosynthesis of INPs by using *Amaranthus dubius* leaf extract (32).

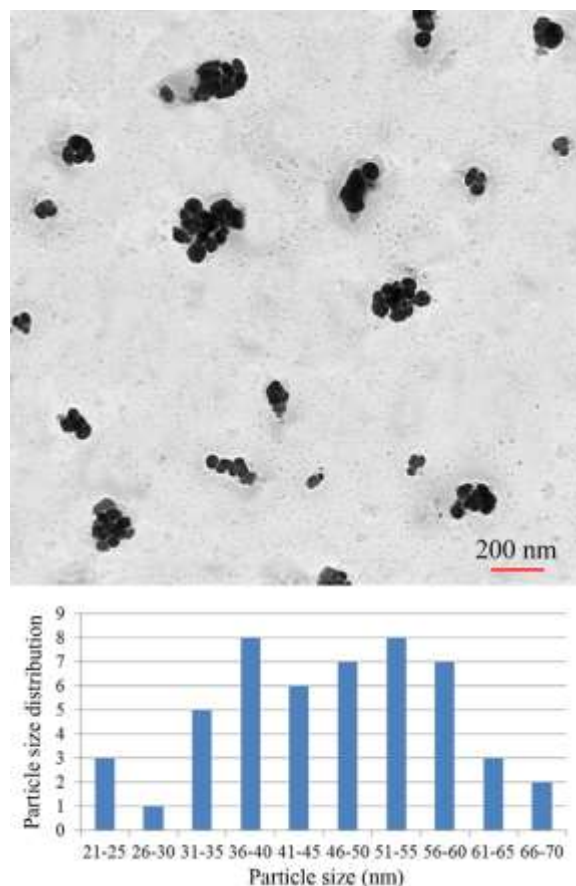


Figure 5: TEM image of the biosynthesized INPs and corresponding particle size distribution pattern

It has been shown that at increased temperatures up to 37°C leaf extract has a higher reduction potential for INPs biosynthesis. But, increase in the reaction temperature above 37°C have a negative effect on the formation of INPs (32). Negative effects of increased temperatures on the bioreduction of metallic ions were also reported for *Zataria multiflora* leaf extract, *Alcea rosea* flower extract and *Ephedra intermedia* stem extract (25, 26, 30). These results indicate that increase in the reaction temperature can degrade plants antioxidant compounds and decreases amount of the reduced nanoparticles (34-37).

Effect of reaction time on the production of INPs was evaluated from 12 h to 48 h. As depicted in Figure 4, increase in the reaction time has no effect on the amount of synthesized nanoparticles. To provide enough time for biological interactions time periods below 12 h are not commonly set for biosynthesis reactions (11, 12, 19, 25, 26, 29, 30). But, there is a report that 90 min is sufficient to achieve highest efficiency in production of INPs by using *Amaranthus dubius* leaf extract (32). Reaction times more than 48 h usually associated with the waste of time, aggregation of nanoparticles, and production of multi-

shaped nanoparticles (38-41).

3.2 Characterization of INPs

TEM micrograph of the INPs is provided in Figure 5.

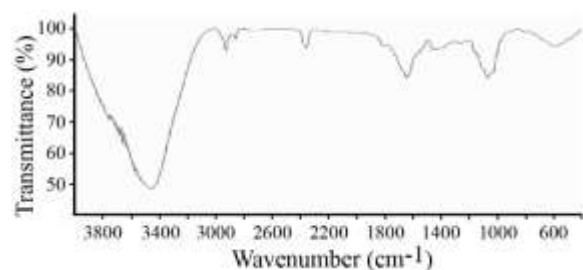


Figure 6: FTIR spectrum of the biosynthesized INPs

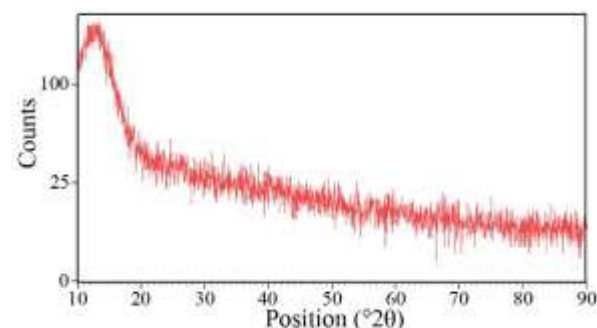


Figure 7: XRD pattern of the biosynthesized INPs

Produced nanoparticles were spherical and oval in shape and were measured to be 21–71 nm with mean particle size of 46 nm. INPs with similar particles size distribution were also obtained by using *Eucalyptus tereticornis*, *Melaleuca nesophila* (42), *Zataria multiflora* (26), pistachio (43), green tea (44-46), and eucalyptus (47). TEM investigations revealed that prepared particles tend to form irregular clusters with phytochemicals from leaf extract and form macrostructures in the range of 117–605 nm. This finding shows the role of plant organic compounds as reducing and stabilizing agent in the synthesis of INPs (43, 48).

Fourier transformed infrared (FTIR) spectroscopy was used as non-destructive way to identify and study the interactions of biological compound with INPs (Figure 6) (49). The broad peak at 3467 cm^{-1} is corresponding to the O–H stretching vibrations (50, 51). The characteristic peak of C–O bond and carbonyl group can be seen at 1070 cm^{-1} and 1636 cm^{-1} , respectively. These functionalities can be corresponding to heterocyclic compounds from proteins and unsaturated hydrocarbons (52-54). Absorption peaks from aliphatic C–H groups are recorded at about 2800 cm^{-1} (55, 56). Fe–O stretching vibration resulted in two characteristic peaks at about 640 cm^{-1} and 450 cm^{-1} . Absence of these peaks in the recorded pattern is an indicative feature for zero-valent INPs (57, 58).

XRD pattern of the synthesized INPs is shown in Figure 7. Lack of distinct diffraction peak shows amorphous nature of prepared nanoparticles. The broad hump peak in the region 10-20 of 2θ degrees is corresponding to organic compounds on the surface of INPs. Similar results were also reported for INPs which synthesized by using eucalyptus leaf

extracts (47), Sorghum bran extracts (59), *Terminalia chebula* (60), and *Syzygium jambos* L. (61).

3.3 Fenton catalytic activity of INPs

Catalytic activity of the prepared nanostructures over 6 h is presented in Figure 8. More than 60 percent reduction in the dye concentration was achieved after 4 h reaction. After 5 h reaction about 70 percent of Methyl orange was degraded and no more significant dye degradation was recorded after this time. Similar time dependent degradation pattern was also reported for other iron nanostructures which synthesized by using green tea leaves extract and leafy branches extract of Mediterranean cypress (*Cupressus sempervirens*) (12, 62).

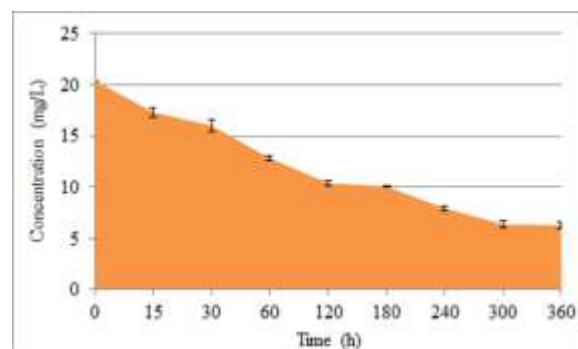


Figure 8: Methyl orange degradation pattern using INPs as Fenton catalyst

4 Conclusions

U. dioica is a potential plant for biosynthesis of metallic nanoparticles. Nettle leaf extract has a significant reduction potential which can reduce ferric ions to zero-valent INPs in a sustainable, economic, and facile manner. Also, it has phytochemicals which can act as biological stabilizer. Reaction conditions (i.e. ferric ion concentration, leaf extract quantity, and reaction temperature) have a significant impact on the bioreduction of INPs. Bioactive compounds in the plants are sensitive to increased temperatures and usually bioreduction reactions are well done at room temperatures. Also, high concentrations of metal precursor can prevent formation of nanoparticles. Increase in the plant extract quantity resulted in the increase in the formation of nanoparticles which is due to increase of bioactive compounds in the reaction. About 12 h of reaction time can be sufficient for the formation of INPs and biological interactions. The particles were efficient as a Fenton-like catalyst and can be developed for technical applications in future.

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Ethical issue

Authors are aware of, and comply with, best practice in publication ethics specifically with regard to authorship (avoidance of guest authorship), dual submission, manipulation of figures, competing interests and compliance

with policies on research ethics. Authors adhere to publication requirements that submitted work is original and has not been published elsewhere in any language.

Competing interests

The authors declare that there is no conflict of interest that would prejudice the impartiality of this scientific work.

Authors' contribution

All authors of this study have a complete contribution for data collection, data analyses and manuscript writing.

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