# How Green is the Green Synthesis of Iron Nanoparticles Using Eysenhardtia polystachya?

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**ABSTRACT:** Nanotechnology is a relatively new discipline that holds promise for soil and water remediation. In recent years the so called green synthesis of nanoparticles (NPs) has received great attention because it could be more economic and generate less toxic compounds than conventional synthesis methods. The objectives of this work were: (i) to evaluate the effects of exposure to atmosphere and the initial concentration of the precursor salt FeCl<sub>3</sub> · 6H<sub>2</sub>O on the yields of NPs by a green synthesis method that used plant extracts of Eysenhardtia polystachya (Palo Azul, Spanish name) as well as NPs characteristics; and (ii) to determine the pollution load of the spent liquors from this socalled green synthesis of the NPs. Ethanol extractions of Eysenhardtia polystachya (Palo Azul, Spanish name; Kidneywood, English name) under atmospheric conditions (A) and inert conditions (N<sub>2</sub> atmosphere, N) were carried out at lab scale. FeCl<sub>3</sub>  $\cdot$  6H<sub>2</sub>O was used as a precursor for the synthesis, at two concentrations, namely 0.10 (1) and 0.16 M (h). The obtained yields of the NPs synthesis (basis Fe in NP/Fe in precursor salt) were very low, *i.e.*, 0.2302; 0.1381; 0.1150; 0.2072, and 0.1842% for (A,I), (A,h), (N,I), and (N,h) conditions, respectively. Scanning electron microscope (SEM) suggested sphericallyshaped nanoparticles with average diameter of 40.44 nm. However, Transmission electron microscopy analysis (TEM) showed tube/rod structures of 39.83 nm of length and 3.31 nm of diameter. Energy dispersive spectroscopy (EDS) coupled to SEM analysis confirmed the presence of oxygen in the NPs. The infrared spectrum of NPs by Fourier Transform (FT-IR) showed the characteristic pattern for magnetite (Fe<sub>3</sub>O<sub>4</sub>). Spent liquors from NPs synthesis had a very low (aggressive) pH of 1.82 well below the interval 5-8 allowed by Mexican regulations whereas the electrical conductivity was 14.25 mS cm<sup>-1</sup>, that is, 4.75 times higher, respectively, than the maximum values allowed for wastewater discharges in Mexico. In addition, the spent liquors exhibited an average chemical oxygen demand of 326 400 mg L<sup>-1</sup>, which far exceeds the maximum allowed value of the Mexican discharge limit of this parameter. These features along with high values of indices (L wastewater/ g NP synthesized),  $\gamma$  (kg COD/g NP synthesized),  $\mu$  (L MeOH/ g NP synthesized),  $\epsilon$  (L EtOH/ g NP synthesized), and  $\phi$  (kg waste Fe/g NP synthesized) strongly suggest that the denomination of "green" to this method and similar procedures should be re-considered.

Keywords: environmental impact, green-synthesis, magnetite, nanoparticles.

## INTRODUCTION

Since 1998 with the publication of Anastas and Warner about the 12 principles of the green chemistry, added to this the global warming and environmental issues around the world, carrying out chemical reactions in a green manner has become an important goal for chemists and modern practice of Chemistry (Lancaster, 2016). Green chemistry looks forward to reduce or eliminate the use of hazardous substances in a chemical process or the generation of hazardous or toxic intermediates or products. It also includes the use of

sustainable raw material and energy sources for this manufacturing process (Doble & Kumar, 2007). Anastas and Warner (1998) published a list with the twelve principles of green chemistry, as shown below:

- 1. *Prevention:* It is better to prevent waste that to treat or clean up waste after it is formed.
- 2. <u>Atom Economy</u>: Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
- 3. <u>Less Hazardous Chemical Syntheses:</u> Wherever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
- 4. <u>Designing Safer Chemicals</u>: Chemical products should be designed to preserve efficacy of function while reducing toxicity.
- 5. <u>Safer Solvents and Auxiliaries:</u> The use of auxiliary substances (e.g. solvents, separation agents, etc.) should be made unnecessary wherever possible and, innocuous when used.
- 6. <u>Design for Energy Efficiency:</u> Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.
- 7. <u>Use of Renewable Feedstocks:</u> A raw material or feedstock should be renewable rather than depleting wherever technically and economically practicable.
- 8. <u>Reduce Derivatives:</u> Unnecessary derivatization (blocking group, protection/deprotection, and temporary modification of physical/chemical processes) should be avoided whenever possible.
- 9. <u>*Catalysis:*</u> Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
- 10. <u>Design for Degradation</u>: Chemical methodologies should be designed so that at the end of their function they do not persist in the environment and break down into innocuous degradation products.
- 11. <u>Real-time analysis for Pollution Prevention:</u> Analytical methodologies need to be developed further to allow for real-time in-process monitoring and control prior to the formation of hazardous substances.
- 12. <u>Inherently Safer Chemistry for Accident Prevention</u>: Substances and the form of a substance used in a chemical process should be chosen so as to minimize the potential for chemical accidents, including releases, explosions, and fires."

In recent years, there has been an important increase in the publication of articles about *NPs* synthesis using green methods based on plant extracts (Table 1), using different precursor salts and solvents. However, to the best of our knowledge, no article has reported so far neither the yield of the synthesis of the *NPs* nor the environmental analysis of its wastes so far.

Therefore, the objectives of this work were: (*i*) to evaluate the effects of exposure to atmosphere and the initial concentration of the precursor salt  $FeCl_3 \cdot 6H_2O$  on the yields of *NPs* by a green synthesis method that used plant extracts of *Eysenhardtia polystachya* (Palo Azul, Spanish name) as well as *NPs* characteristics; and (*ii*) to determine the pollution load of the spent liquors from this so-called green synthesis of the *NPs*.

Plant name and part used	Fabrication method	Characteristics of the nanoparticles	Application of nanoparticles	Ref.
<b>Absinthe</b> <i>Artemisia absinthium</i> Leaf	Plant extract (in deionized water) mixed with AgNO <sub>3</sub> (2 mM), different concentration ratios, at room temperature and different time periods	<i>AgNPs</i> with different shapes in a range of 5 to 20 nm	Antibacterial, antioxidant and cytotoxic activities	1
<b>Pricklypear cactus</b> <i>Opuntia ficus-indica</i> Leaf	Plant extract (in deionized water) mixed with HAuCl₄ (0.01 M) under magnetic stirring at 90°C for 1 hours	Gold <i>NPs</i> with different shapes of 10 to 20 nm in size	Biomedicine, optics and electronics	2
Indian banyan Ficus benghalensis Bark Neem Azadirachta indica Bark	10 mL of plant extract (in deionized water) mixed with 90 mL of AgNO <sub>3</sub> (1 M), at different temperature time periods	Spherical Silver NPs with a size of 40 nm Spherical Silver NPs with an average size of 50 nm	Antimicrobial activity and antiproliferative response against osteosarcoma	3
Cuachalalate Amphipterygium adstringens Bark Liquorice Glycyrrhiza glabra Root	100 μL of plant extract (in 50:50, H <sub>2</sub> O:C <sub>2</sub> H <sub>6</sub> O) dried and diluted with dimethyl sulfoxide DMSO (0.4% final concentration) was added to 25 mL of either 1 mM or 10 mM AgNO <sub>3</sub> . During the reaction the pH was adjusted to 11 using 3.0 M NaOH an	Spherical Silver <i>NPs</i> with a size of 3 nm Spherical Silver <i>NPs</i> with a size of 9 nm	Bactericidal and antimycotic activities against oral microbes	4
<b>Cardus marianus</b> <i>Silybum marianum L.</i> Seed	stirred for 15 minutes 1,0 g FeCl <sub>3</sub> ·6H <sub>2</sub> O and 0.2 g CuCl <sub>2</sub> ·2H <sub>2</sub> O were dissolved in 35 mL of seeds extract (in double distillated water) at 60°C under vigurous stirring for 5 h. During the process the pH was adjusted to obtain alkaline pH, with 0.5 M Na <sub>2</sub> CO <sub>3</sub>	Cu/Fe3O4 <i>NPs</i> with a range of 8.5 to 60 nm	Catalyst for the reduction of nitroarenes	5

TABLE 1. Nanoparticle fabrication by using plant extracts.

		1		1
Plant name and part used	Fabrication	Characteristics of the NP	Application	Ref.
<b>Pomelo fruit</b> <i>Citrus maxima</i> Peel	Plant extract (in ultrapure water) was added to 0.1 M FeCl₃·6H₂O in a 3:1 volume ratio at room temperature	Zero Valent Iron <i>NPs</i> in a range of 10 to 100 nm	Treatment of Cr(VI) solutions.	6
<b>Banana</b> <i>Musa × paradisiaca</i> Peel	1 mL of Peel extract (in distilled water) was mixed with 50 mL of AgNO <sub>3</sub> (1 mM), in the dark at 30°C	Spherical Silver <i>NPs</i> with an average size of 27.9 nm	Antibacterial Activity	7, 8
<b>Caterpillar tree</b> <i>Plumeria alba</i> Flower	10 mL of flower extract (in double distilled water) was mixed with 70 mL of AgNO <sub>3</sub> (1 mM) and incubated for 30 minutes at room temperature	Spherical Silver <i>NPs</i> with an average size of 36.19 nm	Catalytic and various biological activities	9
<b>Cape Jasmine</b> Gardenia jasminoides Leaf	50 mL of plant extract (in deionized water) was	Hexagonal Iron <i>NPs</i> with an average size of 32 nm	Antibacterial Activity	10
<b>Henna</b> <i>Lausonia mermis</i> Leaf	mixed with 10 mL of 0.1 M FeSO₄ (2 ml/5 min), and stirred at 70°C	Hexagonal Iron <i>NPs</i> with an average size of 21 nm	Antibacterial Activity	
<b>Eucalyptus</b> <i>Eucalyptus</i> Leaf	50 mL of plan extract (in desionized water) was injected into 50 mL of 5 mM FeSO4 and 1 mM βCD. The solution was stirred for 0.5 hours	Amorphus Iron <i>NPs</i> with an average size of 57.6 ± 17.4 nm	N.D.	11
<b>European black elderberry</b> <i>Sambucus nigra</i> Fruit	<ul> <li>16.6 mL of plant extract</li> <li>(in food grade acetone and double distilled water) were added to a boiling solution of 6.6 mL</li> <li>1% AgNO<sub>3</sub> in 200 mL double distilled water; and vigourosly stirred for 10 minutes</li> </ul>	Spherical <i>AgNPs</i> in a range of 20 to 80 nm	Anti-inflammatory activity	12
<b>Elephant apple</b> <i>Feronia elephantum</i> Leaf	100 mL of plant extract (in distilled water) were added to 125 mL of 1 mM AgNO <sub>3</sub> and incubated at room temperature	<i>AgNPs</i> with different shapes with an average size of 32 nm	Adulticidal properties against filariasis, malaria, and dengue vector mosquitoes	13

TABLE 1. Nanoparticle fabrication by using plant extracts (Continued).

Plant name and part used	Fabrication	Characteristics of the NP	Application	Ref.
<b>Barley</b> <i>Hordeum vulgare</i> Leaf	Plant extract (in distilled water) was mixed with 0.1 M FeCl₃·6H₂O in a 1:1 ratio at room	Amorphus Iron <i>NPs</i> with an average size of 30 nm	Fenton catalyses	14
Common sorrel Rumex acetosa Leaf	temperature for 30 minutes	Amorphus Iron <i>NPs</i> with an average size of 40 nm		
<b>Sweet flag</b> <i>Acorus calamus</i> Rhizomne	Plant extract (in distilled water) was mixed with AgNO <sub>3</sub> (1 mM) in a ratio of 1:5 and incubated at room temperature for 24 hours	<i>AgNPs</i> with different shapes with an average size of 31.83 nm	Antibacterial activity	15
<b>Black tea</b> Camellia sinensis cultivar: Hunan Xiangbolu Leaf			Degradation of malachite	
<b>Oolong tea</b> Camellia sinensis cultivar: ChinShin Leaf	60 g/L of plant extract (in deionized water) were added to 0.1 M FeSO <sub>4</sub> in a ratio of 1:2	Spherical Iron <i>NPs</i> in a range of 40 to 80 nm	Degradation of malachite	16
<b>Green tea</b> Camellia sinensis Leaf			Degradation of bromothymol blue and malachite	
<b>Sweet wormwood</b> <i>Artemisia annua</i> Leaf	5 mL of plant extract (in distilled water) were added to 95 mL of 0.1 M	N.D.	Antimicrobial, antioxidant and	17
<b>Broomweed</b> <i>Sida acuta</i> Leaf	AgNO <sub>3</sub> , and mixed by manual shaking and placed under sunlight for reduction into <i>AgNPs</i> .	N.D.	corrosion inhibition	
<b>Jiwanti</b> <i>Leptadenia reticulata</i> Leaf	10 mL of plant extract (in methanol) were trated with 90 mL of 1 mM AgNO <sub>3</sub> and incubated at room temperature for 8 hours	Spherical <i>AgNPs</i> in a range of 50 to 70 nm	Biomedical and pharmaceutical applications	18

TABLE 1. Nanoparticle fabrication by using plant extracts (Continued).

Plant name and part used	Fabrication	Characteristics	Application	Ref.
		of the NP		
<b>Mondell Pine</b> <i>Pinus eldarica</i> Bark	250 mL of plant extract (in deionized water) were mixed with AgNO <sub>3</sub> (1, 2, 4, and 6 mM) and phospate buffer (pH = 3, 5, 7, 9, and 11) (final concentrations respectively)	Spherical <i>AgNPs</i> in a range of 10 to 40 nm	Biomedical, pharmaceutical and other applications	19
<b>Bastard oleaster</b> <i>Elaeagnus latifolia</i> Leaf	60 mL of plant extract (in sterilised distilled water) were mixed with 10 mL of 1 mM AgNO <sub>3</sub> and kept at room temperature	<i>AgNPs</i> in a range of 30 to 50 nm	Pharmacological and electronical industries	20
<b>Wormwood</b> <i>Artemisia capillaris</i> Aerial parts	1 mL of plant extract at various concentratios (in both 70% aqueous ethanol or water) were mixed with 1 mL AgNO <sub>3</sub> at various concentratios, and incubated at 80°C for 4 hours	<i>AgNPs</i> in a range of 26 to 30 nm	Antibacterial activities	21
<b>Sweet Cinnamon</b> <i>Cinnamon zeylanicum</i> Bark	100, 500 and 1000 mg of plant powder were added to 50 mL of 1 mM AgNO <sub>3</sub> , and incubated in a rotary shaker at 160 rpm in the dark at 25°C. For aqueous extract, 1, 2.5 and 5 mL of plan extract were added to 50 mL of 1 mM AgNO <sub>3</sub>	Spherical <i>AgNPs</i> in a range of 31 to 40 nm	Bactericidal activity	22

TABLE 1. Nano	particle fabrication	by using plant	t extracts	(Continued)	
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**References**: 1. Ali *et al.* (2016), 2. Álvarez *et al.* (2016), 3. Nayak *et al.* (2016), 4. Rodríguez-Luis *et al.* (2016), 5. Sajadi *et al.* (2016), 6. Wei *et al.* (2016), 7. Ibrahim *et al.* (2015), 8. Bankar *et al.* (2010), 9. Mata *et al.* (2015), 10. Naseem and Farrukh (2015), 11. Zhuang *et al.* (2015), 12. David *et al.* (2014), 13. Veerakumar and Govindaajan (2014), 14. Makarov *et al.* (2014), 15. Nakkala *et al.* (2014), 16. Huang *et al.* (2014), 17. Johnson *et al.* (2014), 18. Swamy *et al.* (2014), 19. Iravani and Zolfaghari (2013), 20. Phanjom *et al.* (2012), 21. Park *et al.* (2012), 22. Sathishkumar *et al.* (2009).

### MATERIALS AND METHODS

**Plant Extracts.** The plant extract was prepared by using *Eysenhardtia polystachya* bark. *Eysenhardtia polystachya* (Ort.) Sarg. (Leguminosae, Lotoideae) is a small tree distributed in Mexico, with diuretic properties, used as a treatment of kidney and bladder infections (Beltrami et al., 1982; Burns et al., 1984).

The bark was cut into small pieces of 0.2 cm side average. For both the under environmental conditions extract (*A*) and under inert conditions extract (*N*), distilled water (dH<sub>2</sub>O) and absolute ethanol were added to the small pieces of bark at a ratio of 1:16:16 (w/v/v). The extract under inert conditions was flushed with a constant N<sub>2</sub> gas flow during the complete procedure. Both extracts were maintained in darkness, with constant mixing and a temperature of 80°C for 40 min until centrifugation for 15 min at 2500 rpm. Afterwards, supernatants were filtered by using 0.22 µm filters (Millipore). The filtered extract under inert conditions was stored in a dark vial with Teflon<sup>®</sup> cap, and then the headspace flushed with N<sub>2</sub> gas.

**Experimental design and procedures for nanoparticles synthesis.** The effects of two factors on nanopaticle synthesis were tested, namely, the initial concentration of the iron salt (low and high, 0.10 and 0.16 M, *I* and *h* respectively) and the atmosphere in contact with reaction vials (atmospheric air and inert N<sub>2</sub> headspace, *A* and *N*, respectively). This design gave a total of four combinations or "treatments".

To synthesize *Fe NPs*, 30 mg of sodium dodecyl sulfate was suspended in 2 mL of methanol. For the 0.10 M experimental design (low concentration of precursor salor (or *I*), 4.5 mL of an aqueous solution of 0.5 M Iron (III) chloride (FeCl<sub>3</sub>  $\cdot$  6H<sub>2</sub>O) and 3.5 mL of dH<sub>2</sub>O were added into the main solution; whereas for the 0.16 M experimental design (high concentration of precursor salt (or *h*), 7.5 mL of the aqueous solution of 0.5 M Iron (III) chloride (FeCl<sub>3</sub>  $\cdot$  6H<sub>2</sub>O) and 0.5 M Iron (III) chloride (FeCl<sub>3</sub>  $\cdot$  6H<sub>2</sub>O) and 0.5 mL of dH<sub>2</sub>O were added into the mixture. After, 5 mL of *Eysenhardtia polystachya* bark extract were carefully added by a ratio of one drop per second, whilst the solution was being mixed. The color of the solution immediately turned from pale yellow to dark as a response to the reduction. The mixture was kept under constant shaking at 37°C for 1 hour. The samples were centrifuged at 1,500 x g for 10 min. The supernatant (spent liquor) was removed and kept in a container for further analysis. The nanoparticles were rinsed 10 times by adding 1 mL of methanol, shaking the sample for 1 minute with a vortex, and centrifuging at 1,500 x g for 10 min. The supernatant obtained after every rinse (flush) was kept in a container for further analysis.

The yield of the nanoparticles synthesis was calculated using the Equations 1 to 3 shown below:

$$M_{FeSS} = C * MA_{Fe} * V_{Ext}$$
<sup>[1]</sup>

$$M_{FeNP} = M_{NP} * \frac{3 M A_{Fe}}{F W_{Fe_3} o_4} * \frac{1}{0.015}$$
[2]

$$\eta_{Synthesis} = \frac{M_{FeNP}}{M_{FeSS}} * 100$$
[3]

where  $\eta_{Synthesis}$ , synthesis yield (g Fe in vial/g Fe in *NP*, %);  $M_{FeSS}$ , initial mass of iron in the solution in the reaction vial; *C*, initial concentration of the precursor salt (M);  $MA_{Fe}$ , atomic weight of Iron (g/mol);  $M_{FeNP}$ , Mass of Fe in the *NP* (g);

 $M_{NP}$ , Mass of synthetized NPs (g); FW<sub>Fe<sub>3</sub>O<sub>4</sub></sub>, Formal weight of magnetite (g/mol); V = Volumen of liquor in the reaction vial (L)

**Nanoparticles Characterization.** The shape and size of the iron nanoparticles was determined in a scanning electron microscope (*SEM*) FE HRSEM Auriga-3916, operating at 30 kV. The shape of the nanoparticles at a shorter length was determined by Transmission Electron Microscopy (*TEM*), by loading a drop of these on a copper grid, and dried at room temperature; likewise, the elemental composition of the nanoparticles was determined by energy-dispersive X-ray spectroscopy (*EDS*) coupled to the Transmission Electron Microscope (JEOL-ARM200F) mentioned before, operated at 120 kV. Fourier transform infrared spectroscopy (*FT-IR*) analysis was carried out using dried nanoparticles set on the sample holder of a Two<sup>TM</sup> IR spectrometer.

**Environmental analysis of the spent liquors.** The pH analysis of the spent liquors was carried out with the usage of a Beckman  $\phi$  41 pH meter, by introducing the electrode into a flask with 20 mL of each spent liquor. The chemical oxygen demand (COD) test was carried out according to the method published by Knechtel (1978). The electrical conductivity of the spent liquors was analyzed using a HI-8633 Multi-range Conductivity Meter.

**Chemicals.** Iron (III) chloride was purchased from Reactivos Química Meyer (Química Suastes S.A. de C.V.). Bark of *Eysenhardtia polystachya* (Palo Azul, Spanish name; Kidneywood, English name) was purchased at the market "El Sonora" in Mexico City, Mexico.

## **RESULTS AND DISCUSSION**

**Nanoparticles Synthesis Yield.** The yield of the nanoparticles synthesis was very low (**Table 2**). On average, per every 5 mL of extract and 10 mL of precursor salt, 0.4 mg of nanoparticles were typically obtained. There were no clear effects of either inert versus atmospheric factor and precursor salt concentration factor on the *NP* yield.

Plant extract obtained with vials exposed to the atmosphere ( <i>A</i> )		Plant extract continuous ga	obtained under assing with N <sub>2</sub> ( <i>N</i> )
FeCl <sub>3</sub> [0.10 M]	FeCl₃[0.16 M]	FeCl₃ [0.10 M]	FeCl₃[0.16 M]
(1)	(h)	(1)	(h)
0.2302	0.1381	0.1150	0.2072

TABLE 2. Yield of the nanoparticles synthesis (%).

Low yields probably will determine that the quantity of waste generated in terms of gram of fabricated *NP* would result too high, and this, in turn, could become a very negative (and contradicting) characteristic of this "green" method.

**Nanoparticles Characterization.** *SEM* micrographs showed the morphology of the nanoparticles was nearly as shown in Figure 1 and Figure 2 with average diameters of 44.80, 39.83, 33.99 and 40.70 nm r for the four treatments (*A*,*I*); (*A*,*h*); (*N*,*I*), and (*N*,*h*), respectively. However, the images obtained by *TEM* showed that the morphology was

nanotubes of average length of *NP*s 39.83 nm by average diameter of 3.31 nm (Figure 3 and Figure 4).



FIGURE 1. SEM micrographs of the synthesized nanoparticles. A. [A, l]; B.[A, h]; C.[N, l]; D. [N, h]; E. Color change of the precursor salt upon iron nanoparticles formation.

![](_page_8_Figure_4.jpeg)

FIGURE 2. Histograms and frequency polygons of the sizes obtained by the *SEM* micrographs of the synthesized nanoparticles. A. [A, l]; B.[A, h]; C.[N, l]; D. [N, h].

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![](_page_9_Figure_1.jpeg)

FIGURE 3. *TEM* micrographs of the magnetite nanoparticles obtained at different scales and electron diffraction pattern showing the crystal planes of magnetite.

![](_page_9_Figure_3.jpeg)

FIGURE 4. Histograms and frequency polygons of the sizes obtained by the *TEM* micrographs of the synthesized nanoparticles. A. [A, l]; B.[A, h]; C.[N, l]; D. [N, h].

The *EDS* analysis (Figure 5) demonstrated the presence of iron and oxygen in the nanoparticles, information that compared to the diffraction pattern obtained in *TEM* and the results showed in *FT-IR* (Figure 6), confirmed the presence of magnetite in the nanoparticles, with the specific vibrations of the Fe-O bond at 640 cm<sup>-1</sup> (Ardelean and Timar, 2008; López et al., 2010).

![](_page_10_Figure_2.jpeg)

FIGURE 5. Energy-Dispersive X-ray spectroscopy of the magnetite nanoparticles.

![](_page_10_Figure_4.jpeg)

FIGURE 6. Fourier Transform Infrared Spectroscopy (FT-IR) of the synthesized nanoparticles.

Environmental analysis of the spent liquors. The greater the chemical oxygen demand values are, the greater is the pollution and the risks faced by the uncontrolled discharge of

the wastewater (Sincero & Sincero, 2003). Taking into account this statement, and observing that the values exceeded the range of extremely contaminated water (200 mg BOD/L daily average) that is used in agriculture irrigation as well as the Mexican regulations for wastewater discharge as shown in the Official Mexican Norm 001 (SEMARNAT, 1996), the wastes generated during the nanoparticles synthesis can be judged as highly contaminant (Table 3).

Sample type	Treatment or	COD	BOD₅
	Condition	(mg O <sub>2</sub> /L)	(mg O <sub>2</sub> /L)
Spent Liquor	A, I	342'400 ± 20'544	174´972 ± 18´384
Spent Liquor	A, h	329'600 ± 0.0	201′472 ± 19′091
Spent Liquor	N, I	307'200 ± 18'432	208´972 ± 9´899
Spent Liquor	N, h	326'400 ± 19'584	214′972 ± 38′183
Methanolic washing	A, I	1'292'800 ± 0.0	N/A
Methanolic washing	A, h	1'139'200 ± 0.0	N/A
Methanolic washing	N, I	1'209'600 ± 72'576	N/A
Methanolic washing	N, h	1'388'800 ± 138'880	N/A

TABLE 3. Chemical oxygen demand and biochemical ox	kygen demand of the wastes.
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N/A: Not Applicable, methanolic washings will be distilled for solvent recovery.

Biochemical oxygen demand  $BOD_5$  of effluents, that is, organic matter that is biodegradable, was consistently high for all the treatments or conditions (Table 3). According to the  $BOD_5$  values obtained, it seems that the wastes generated by the synthesis of nanoparticles using extracts obtained under inert conditions (*N*) exhibited higher  $BOD_5$  than those generated by the procedure where the samples were exposed to the atmosphere (*A*) (Table 3). Similarly, spent liquors that were concocted with the high concentration of iron salt showed higher  $BOD_5$  than those liquors made with low concentration of FeCl<sub>3</sub>.

A rapid inspection of Table 3 shows that the relation  $BOD_5/COD > 0.7$  for the spent liquors. It is known that for ratios lower than 0.2, the organic matter content of the effluent is judged as recalcitrant. When the ratio is higher than 0.6, the organic matter in the effluent is considered to be biodegradable. That is, amenable to biological treatment (Lapeña, 1990). In our case, the spent liquors can be treated by biological methods in order to abate their pollutant load. We recommend to explore first anaerobic (methanogenic) treatment, as a way to provide simultaneously treatment and energy recovery (Poggi-Varaldo & Rinderknecht, 1996).

Electrical conductivity gives and estimation of the soluble salts dissolved in an effluent. Besides, in case the wastes were discharged to soil or water bodies, it might by risky, since it can cause problems of salinization, drainage, evaporation, drought and solvation (Burt, 2014). In the case of the wastes obtained from the synthesis, all spent liquors exhibited high electrical conductivities (Table 4), which means a high quantity of ions from salts. Likely, the source of ions is the FeCl<sub>3</sub> and its hydrolysis products. In the case of the methanolic washings, as it was expected, conductivities were null (Table 4).

As it can be seen in Table 4, the pH of the wastes is highly acid, indicating that all the residues need special conditioning before any treatment or discharge is attempted. Particularly, because of low values of pH coupled to high values of conductivity, the effect on soil would be devastating: soil salinization and acidification, remobilization of heavy metals that could be precipitated or sequestered into the normal soil, negative impacts on

soil microflora (thus disrupting nutrient biogeocycles), *etc.* Besides, at the pH of Table 4, the effluents become very aggressive/corrosive to a wide range of construction materials (concrete, mortars, metallic pipes, metallic equipment, etc.). The values of pH are well below the permissible range set by the Mexican regulations (NOM-001-SEMARNAT-1996) that are values of pH between 5-10.

Waste	Condition/Treatment	Electrical conductivity (mS/cm)	рН
Spent Liquor	A, I	13.7 ± 0.79	1.94 ± 0.069
Spent Liquor	A, h	17.9 ± 1.03	1.77 ± 0.027
Spent Liquor	N, I	14.8 ± 0.85	1.86 ± 0.018
Spent Liquor	N, h	20.1 ± 1.16	1.73 ± 0.009
Methanolic washing	A, I	< DL	2.01 ± 0.011
Methanolic washing	A, h	< DL	1.97 ± 0.045
Methanolic washing	N, 1	< DL	2.11 ± 0.048
Methanolic washing	N, h	< DL	2.04 ± 0.065

TABLE 4. Electrical conductivity and pH of the wastes.

Notes: DL: detection level.

Table 5 displays the values of several pollution indicators of the examined method. All values were very high, undoubtedly related to the low amount of *NP* harvested (i.e., low yields, Table 2). Particularly the high values of  $\mu$ ,  $\omega$ , and  $\phi$  suggest on the one hand a strong, negative environmental impact if the spent liquors are discharged to water bodies or soils; on the other hand these indicators point out to the need of treating spent liquors, thus increasing costs and decreasing sustainability of the synthesis method. The indicators (L MeOH/ g *NP* synthesized) and (L EtOH/ g *NP* synthesized) show that solvent usage is prohibitively high (Table 5), and likely recovery of both methanol and ethanol from the current synthesis method is mandatory. Yet, this recovery would be energetically intensive and expensive. For instance, waste solvents should be distilled (in order to recover MeOH and EtOH that could be reused) and this unit operation is known to be energetically intensive (standard enthalpies of evaporation are 1129 and 839.31 kJ/kg for MeOH and EtOH, respectively).

# TABLE 5. Pollution indicators of the synthesis of iron nanoparticles using Palo Azul

Indicator	Value
ω (L wastewater/ g NP synthesized)	24
γ (kg COD/g <i>NP</i> synthesized)	7.09
μ (L MeOH/ g <i>NP</i> synthesized)	17
ε (L EtOH/ g <i>NP</i> synthesized)	4
$\phi$ (g waste Fe/g <i>NP</i> synthesized):	
0.10 M	32

extracts.

0.16 M	53

The high values of indicators in Table 5, along with large COD and BOD values and corrosive/aggressive pHs of effluents, strongly suggest that the denomination of "green" to this method and similar procedures should be re-considered.

### CONCLUSION

The yield of the nanoparticles synthesis was very low (0.1726% in average). There was no clear effects of either inert vs atmospheric factor and precursor salt concentration factor on the *NP* yield. *TEM* showed that the morphology was nanotubes of an average length of *NP*s 39.83 nm by average diameter of 3.31 nm. The *EDS* analysis demonstrated the presence of Iron and Oxygen in the *NP*s; this was confirmed by *FT-IR*. Moreover, *FT-IR* also showed that *NP* material was magnetite.

With the environmental results obtained in this study, it can be inferred that the fabrication of iron nanoparticles using extracts of *Eysenhardtia polystachya* (Palo Azul) does not qualify as a green technique, since it generates a huge amount of wastes that can be very harmful for both human health and the environment. Indeed, the methods fails to fulfill several principles of the green chemistry as stated by Anastas and Warner, i.e., "(1) Prevention" and "(2) Atom economy, since it generates a great amount of waste". The environmental analysis also showed how hazardous and toxic the generated wastes can be, failing to accomplish principles three and four, "(3) Less hazardous chemical syntheses", and "(4) Designing safer chemicals". As mentioned above, the synthesis and cleaning nanoparticles in this method used ethanol and methanol that contributed to waste generation. Particularly methanol is known to be toxic to humans, failing to accomplish principle number five, namely "(5) Safer solvents and auxiliaries."

Recovery of both ethanol and ethanol from the current synthesis method would be energetically intensive and expensive. Separation of waste iron (III) and further treatment of the spent liquors (either biological treatment or other phys-chem treatments) before discharge would add to the non-sustainability of the use of this plant extract for iron-based nanoparticles synthesis.

We strongly claim that all the methods of *NP* synthesis already published in the open literature based on plant extracts should be re-analyzed in terms of the yields of *NP* and the pollution indicators used in our work (and others) in order to determine their true feasibility and sustainability, and these results should be reported along with the characteristics and applications (if any) of the *NP*s.

### ACKNOWLEDGEMENTS

The authors wish to thank S.N.I. and HMP-V for partial fellowships to C.G. Mar-Pineda. The experimental work was partially supported with personal funds of HMP-V. The authors are grateful to Dr. Daniel Bahena-Uribe and Dr. Jorge Roque-de-la-Puente from Laboratorio de Nanotecnología Avanzada (LANE CINVESTAV-IPN) for their excellent technical help with characterization of nanoparticles (*SEM*, *TEM*, *EDS*), Dr. Marco A. Leyva Ramírez for the *XRD* analysis (Dept. of Chemistry) as well as Dr. Omar Solorza-Feria and Ms Miriam M. Tellez Cruz (Dept. of Chemistry of CINVESTAV-IPN) for their help with *FT-IR* analysis.

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# NOTATION

- A, I Plant extract obtained with vials exposed to air and FeCl<sub>3</sub>·6H<sub>2</sub>O [0.10 M]
- A, h Plant extract obtained with vials exposed to air and FeCl<sub>3</sub> [0.16 M]
- BOD<sub>5</sub> Biochemical oxygen demand
- COD Chemical oxygen demand
- EDS Energy dispersive spectroscopy
- EtOH Ethanol or ethyl alcohol
- *FT-IR* Fourier transform infrared spectroscopy
- MeOH Methanol or methyl alcohol
- *N, I* Plant extract obtained under continuous gassing with inert N<sub>2</sub> and FeCl<sub>3</sub>·6H<sub>2</sub>O [0.10 M]
- *N*,*h* Plant extract obtained under continuous gassing with inert N<sub>2</sub> and FeCl<sub>3</sub>·6H<sub>2</sub>O [0.16 M]
- NP Nanoparticle
- SEM Scanning electron microscopy / Scanning electron microscope
- TEM Transmission electron microscopy / Transmission electron microscope
- XRD X-ray diffraction

# Greek characters

- ε L EtOH/ g NP synthesized
- $\gamma$  kg COD/g *NP* synthesized
- $\eta$  Yield
- $\mu$  L MeOH/ g *NP* synthesized
- $\phi$  g waste Fe/g *NP* synthesized
- *ω* L wastewater/ g *NP* synthesized