

Green synthesis of NiO NPs using the aqueous extract of *Drimia maritima* and investigation of its catalytic activity for removal of aromatics from the natural water sources of Soran city

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Abstract

The NiO nanoparticles (NPs) were biosynthesized using the aqueous extract of the *Scilla Martitimal* (*Drimia maritima*) from the family of *Asparagaceae*. The green synthesized NiO NPs was characterized using electron dispersive spectroscopy (EDS), Uv-vis spectroscopy (Uv-vis), X-ray diffraction (XRD), scanning electron microscopy (SEM) and elemental mapping. Furthermore, the excellent catalytic activity, of green synthesized nanoparticles was monitored using Uv-vis spectroscopy during the removal of aromatic contaminants from the water resources of northern parts of Soran city of Iraqi Kurdistan at ambient temperature.

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1.Introduction

In last decades nanomaterials attract the interest of many researchers due to their different physicochemical characteristics from the bulk materials. These exclusive properties originated from the large surface area of nanoparticles which caused to their applications in many areas especially in catalysis, [1, 2]. Among the nanomaterials nickel oxide nanoparticles is a valuable nanostructure due to its useful electronic, magnetic and catalytic properties [3, 4]. However, to our knowledge, no report was presented about the application and potential of NiO NPs in removal of aromatics from the real water samples. In this study an ecofriendly method was used to obtain NiO NPs using the aqueous extract of *Drimia maritima*. Green technology covers a broad area ranging from production to consumption which mainly involves the use of environmental technologies for monitoring and assessment, pollution prevention and control, and remediation and restoration. Therefore, tracking those pollutions are essential to measure the release of natural or anthropogenic materials of a harmful nature and also avoid the production of environmentally hazardous substances or alter human activities in ways that minimize damage to the environment. Furthermore, both controlling the hazardous and dangerous substances before entering the environment and also improving the condition of ecosystems, degraded through naturally induced or anthropogenic effects as remediation process of green nanotechnology [5-7]. Among the pollutions, aromatic compounds are the main pollutants with considerable hazards to living systems. Polycyclic aromatic hydrocarbons (PAHs) are lipophilic highly soluble compounds in organic solvents including fused aromatic rings with various toxicity produced mainly via incomplete combustion and pyrolysis of materials containing carbon and hydrogen, such as coal, oil, wood and petroleum products. [8, 9]. Many reports confirmed that aromatic compounds especially PAHs are environmentally persistent poisons with carcinogenic, immune suppressant and mutagenic effects. The main sources of poly aromatic compounds are pyrogenic, petrogenic, and biological processes in which those produced from the petrogenic source are most widespread pollutants for considerable transportation, storage and application of crude oil and its products, [10, 11]. *Drimia maritima* (*Scilla Martitimal*) is a species of flowering plant in the family *Asparagaceae*, native to southern Europe, western Asia, and northern Africa. The plant extract is largely used in the traditional medicine for its cardiovascular effects, cytotoxic, antibacterial, antifungal, anti-inflammatory, antioxidant and antiviral activities. According the reported literature about the phytochemical and ethnopharmacological analysis of the plant, its extensive medicinal effect is for presence of a high concentration of phytochemicals such as flavonoids, phenolics, glycosides especially cardiac glycosides, tannins, saponines, alkaloids and carbohydrates, [12-16]. Therefore, during this study the extract of the *Drimia maritima* was used as bioreducing and capping agent to biosynthesis of NiO NPs through a simple, convenient, green, fast and economical method.



Figure1. Image of the *Drimia maritima* (*Scilla Martitimal*) plant

In continuation of our previous studies on green synthesis of nanostructures, [17-23], through this study, the green synthesized NiO NPs using the extract of *Drimia maritima* were absolutely characterized and employed as

bioadsorbent to removal of aromatic contaminations from the water resources of Soran city in Kurdistan region of Iraq.

2. Materials and methods

All reagents and materials used in this process are from Aldrich. All solutions were prepared with distilled water. Glass apparatus and vessels were cleaned by soaking in 10% HNO_3 followed by rinses with distilled water.

2.1. Plant material

The *Drimia maritima* was collected in July 2017 at Sarshive region at Kurdistan province from Iran. Voucher specimen was deposited at the herbarium of Kurdistan natural resources office in Sanandaj, Iran.

2.2. Water samples collection

Soran city is located on latitude of $36^{\circ}39'16.91''$ N and longitude of $44^{\circ}32'16.11''$ E at NE Iraq. Some water resources of the city suffers from the presence of different amounts of aromatics with anthropogenic origine and also biological processes especially those produced from the petrogenic source. A total of 10 surface water samples were collected around the northern parts of the Soran city during April 2018. The samples were collected mainly from the natural and residential area. The location of the samples are demonstrated in Figure 2.



Figure 2; Geological map of water samples locations

2.3. preparation of plant extract

50 g of dried root powder of the plant was heated in 500 mL distilled water for 40 minutes at 80°C then the aqueous extract was filtered and kept in refrigerator for further steps of the study.

2.4. Biosynthesis of NiO NPs using the root extract of *Drimia maritima*

In a typical synthesis of NiO NPs, 50 mL of the aqueous extract of the plant was added dropwisely to 50 mL of well-mixed 0.005 M aqueous solution of $\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$ with constant stirring at pH 9 and 80°C . After 10 min the color of the solution was changed due to excitation of surface plasmon resonance which indicates the formation of NiO NPs as monitored using the Uv-vis spectroscopy. The obtained solution of nanoparticles centrifuged at 7000 rpm for 30 min to absolutely separation at room temperature. Finally the obtained NiO NPs was calcined at 500°C for 45 min to its more purification and cristalinity.

2.5. Removal of aromatics from the natural water samples of Soran city

Firstly, 20 mL of each water samples (S_1 to S_{10} , Figure 2) was monitored using the Uv-vis spectroscopy to detect their aromatic contents. After detecting the presence of aromatics inside the samples, all water samples (S_1 to S_{10}) were

mixed together. In next step, 10 mg of Nickel oxide NPs was added to 50 mL of the sample mixtures along with the same volume of freshly prepared aqueous NaBH_4 (5.3×10^{-3} M) while stirring at room temperature. The result then was checked using Uv-vis spectrophotometer.

3. Results and Discussions

3.1. Spectroscopic analysis of the *Drimia maritima* extract

According the Uv-vis spectrum of plant extract, Figure 3, the signals depicted at 315 nm (bond I) and 275 nm (bond II) are assigned to the cinnamoyl and benzoyl phenolic systems. In fact, these signals are related to the $\pi \rightarrow \pi^*$ transitions which demonstrate the presence of phenolics as antioxidant source for green synthesis of nanoparticles.

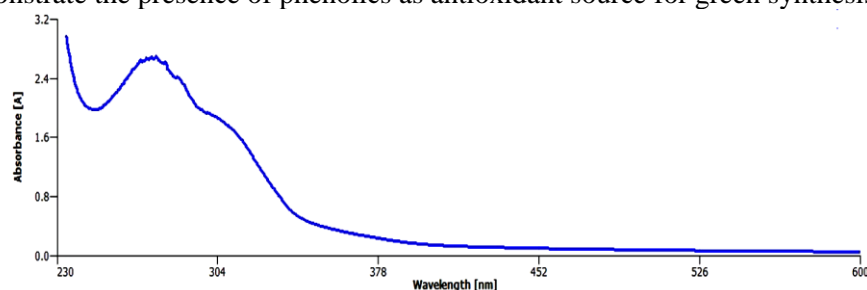


Figure 3. Uv-vis spectrum of *Drimia maritima* extract

3.2. Biosynthesis of NiO NPs

During the biosynthesis of NiO NPs, changing the color of the mixture is a main signal that appears due to surface plasmon resonance around 312 nm showing the formation of NiO NPs. The obtained results about the NiO NPs, had a very good agreement with previously reported literatures. The biosynthesized NiO NPs was characterized using the XRD, SEM, EDS and mapping analytical techniques.

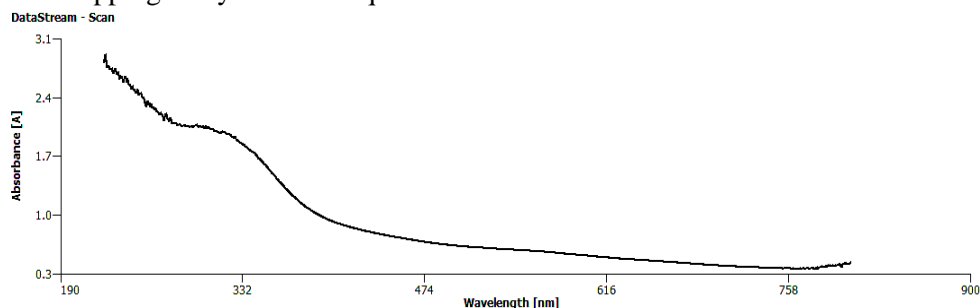


Figure 5. Uv-vis spectra of biosynthesized NiO NPs

The XRD pattern of NiO NPs shows signals at 37.32, 43.41, 63.1, 75.9 and 79.4 degrees assigned to the corresponding 111, 200, 220, 311 and 222 indices which confirms the formation of pure and crystalline NiO NPs, Figure 6.

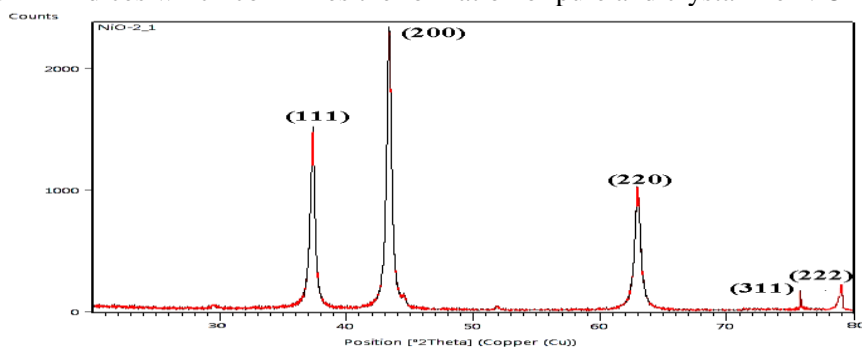


Figure 6. XRD pattern of the green synthesized NiO NPs

The EDS spectrum and elemental mapping of the green synthesized NiO NPs demonstrated the presence of Ni and O elements in the structure of nanoparticles indicating the formation of NiO NPs, Figures 7 and 8.

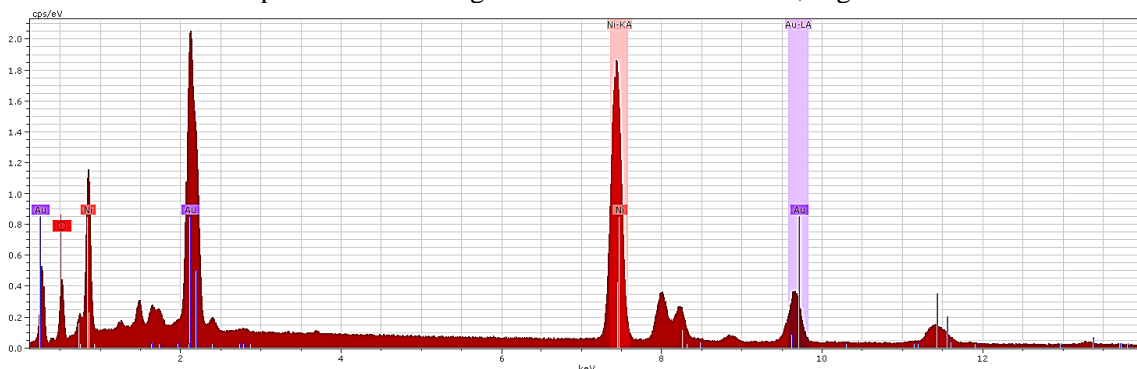


Figure 7. XRD pattern of the green synthesized NiO NPs

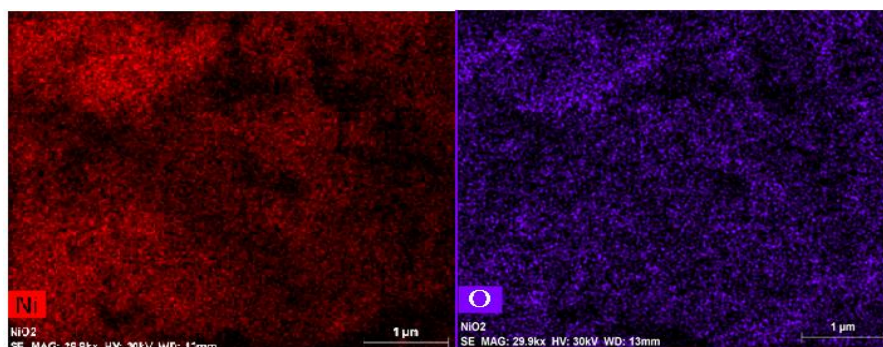


Figure 8. The elemental mapping of green synthesized NiO NPs

The morphological properties of the NiO NPs was screened using FE-SEM analysis. Figure 9 presents the typical FE-SEM images of the nanoparticles at different magnifications. As shown in micrographs, NiO NPs have nearly spherical morphology with some agglomerations and average size ranging 30-60 nm.

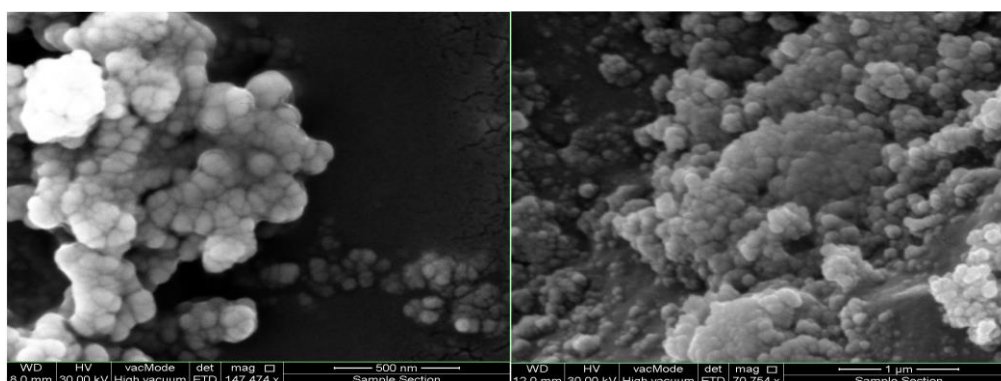


Figure 9. The SEM micrographs of green synthesized NiO NPs

3.3. Adsorption of aromatic contaminations using the NiO NPs

The analysis of sample mixtures (S_1 to S_{10}) using the Uv-vis spectroscopy showed the signals at 205 nm and 235 nm as the main signals of mono aromatic compounds and revealed the presence of aromatic contaminations inside the sample mixture, [24]. Adding 10 mg of Nickel oxide NPs and freshly prepared aqueous NaBH_4 ($5.3 \times 10^{-3}\text{M}$) at room temperature to the samples mixture containing aromatic contaminations caused to disappearing the main signals of mono aromatics inside the water samples and their adsorption after 20 min, Figure 10. Of course, as the NiO NPs

during this study was green synthesized, the plant phytochemicals probably adsorbed on the surface of nanoparticles which beside their protection against the deformation and decomposition processes, they act as capping agents to capture the aromatic contaminations on the nanosurface and increase the synergic effects and rate of aromatics adsorption during the reaction process.

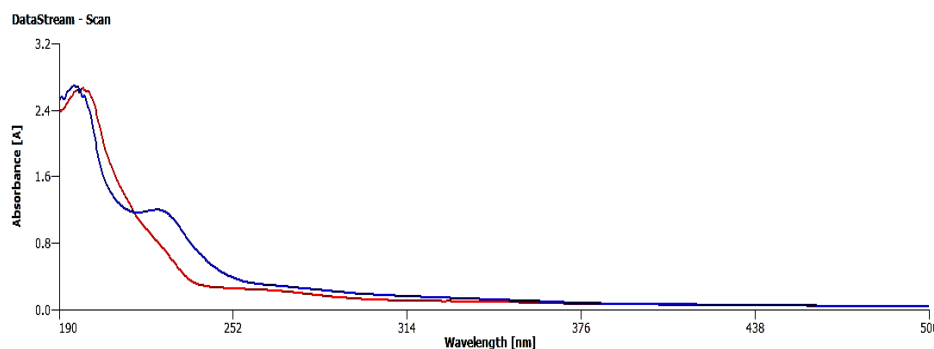


Figure 10. Uv-vis spectrum of the water samples mixture including aromatic contaminations (Blue spectrum) and after its treatment using NiO NPs and NaBH₄ at room temperature.

Table 1. The removal of aromatic contaminations using *NiO* NPs

Entry	Samples (mL)**	NaBH ₄ (M)	Catalyst (mg)	Time (min)
1	50 mL	5.3×10^{-3}	3	55 min
2	50 mL	5.3×10^{-3}	5	35 min
3	50 mL	5.3×10^{-3}	8	25 min
4	50 mL	5.3×10^{-3}	10	20 min
5	50 mL	5.3×10^{-3}	No catalyst	NR*
6	50 mL	0 M	10	NR*

*NR: No reaction, **Mixture of water samples (S₁ to S₁₀)

Moreover, to evaluate the performance of the green synthesized NiO NPs in removal of aromatic contaminations of water sample, the different amounts of nanoparticles were investigated, Table 1. According to Table 1, the best result for the rate of aromatics removal (20 min) was obtained with 10 mg catalyst (NiO NPs), in the presence of NaBH₄ and at room temperature, (entry 4). The removal process of aromatic contaminations using the mentioned conditions was monitored spectrophotometrically by disappearing the maximum absorbance of aromatics. Further, it was demonstrated that in the absence of catalyst (NiO NPs) or NaBH₄, there is no removal reaction occurred in the system, (entries 5 and 6).

4. Conclusion

Through this study a simple and convenient method was employed using NiO NPs to removal of aromatic contaminations of natural water samples of Soran city. The NiO NPs were green synthesized using the aqueous extract of the *Drimia maritima* plant as capping and reducing media and then characterized using the SEM, EDS, XRD, elemental mapping and Uv-vis analysis. The biosynthesized NiO NPs further were applied to removal of aromatic contaminations of water samples of northern parts of the Soran city as monitored using Uv-vis spectroscopy. The green synthesized NiO NPs demonstrated a very good potential in this process at room temperature.

References

- [1] Dingsheng Wang, Run Xu, Xun Wang and Yadong Li, *Nanotechnol.*, 17 (2006) 979–983.
- [2] Kamat P V, *Chem. Rev.*, 93 (1993) 267
- [3] M Nasrollahzadeh, SM Sajadi, M Maham, (2015), *J Mol Cat. A: Chemical.*, 396, 297-303
- [4] Kjabunde K J, Stark J, Koper O, Mohs C, Dong G P, Decker S, Jiang Y, Lagadic I and Zhang D, *J. Phys. Chem.*, 100 (1996) 12142
- [5] S. Baker and S. Satish, *Int. J. Bio-Inorg. Hybd. Nanomat.*, 1 (2012) 67-77.
- [6] D. M. Dubbs, I. A. Aksay, *Ann. Rev. Phys. Chem.*, 51 (2000) 601–622.
- [7] S. Iijima, C.Brabec, A.Maiti, and J. Bernholc, *J. Chem. Physiol.*, 104 (5) (1996) 2089–2092.
- [8] H. I. Abdel-Shafy, M. S.M. Mansour, *Egypt. J. Pet.*, 25 (2016) 107-112.
- [9] J. He, J. J. Li, Y. Wen, H. W. Tai, Y. Yu, W. C. Qin, L. M. Su, Y. H. Zhao, *Chemosphere.*, 128 (2015) 111-118.
- [10] N.D. Dat, M. B. Chang, *Sci Total Environ.*, 609 (2017) 682-691.
- [11] O. E. Orisakwe, Z. N. Igweze, K. O. Okolo, N. A. Udowelle, *Toxicol Rep.*, 2 (2015) 1019-1024.
- [12] Mahbubeh Bozorgi, GholamrezaAmin, Maryam Shekarchi, Roja Rahimi, *J. Trad. Chin Med.*, 37 (2017)124-139.
- [13] J Stannard, *J Urban Health.*, 50 (1974) 684-713.
- [14] FL Chamberlain, RL Levy, *Am Heart J.*, 14 (1937) 268-283.
- [15] DR Climenko, *J Am Pharm Assoc.*, 27 (1938), pp. 596-603.
- [16] Merghoub N, Benbacer L, Amzazi S, Morjani H, El Mzibri M, *J Med Plants Res.*, 3 (2009) 1045-1050.
- [17] M. Nasrollahzadeh, S. M. Sajadi, *J. Colloid Interface Sci.*, 469 (2016) 191-199.
- [18] M. Nasrollahzadeh, S. M. Sajadi, Y. Mirzaei, *J. Colloid Interface Sci.*, 468 (2016) 156-163.
- [19] A. Hatamifard, M. Nasrollahzadeh, S. M. Sajadi, *New J. Chem.*, 40 (2016) 2501-2513.
- [20] S. A. Mahmud, *J. Chem. Pharm. Res.*, 9 (2017) 326-330.
- [21] Z. Issaabadi, M. Nasrollahzadeh, S. M. Sajadi, *J. Colloid Interface Sci.*, 503(2017) 57-64.
- [22] M. Maryami, M. Nasrollahzadeh, E. mehdipour, S. M. Sajadi, *Sep Purif Technol.*, 184(2017) 298-305.
- [23] M. Maham, M. Nasrollahzadeh, S. M. Sajadi, M. Nekoei, *J. Colloid Interface Sci.*, 497(2017) 33-42.
- [24] EO. Odebunmi and SA. Adeniyi, *Bull. Chem. Soc. Ethiop.*, 21 (2007) 135-140.