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Purposeful scientific research as a pillar of sustainable development



Synthesis of Cobalt Nanoparticles Using Two Methods: Physical and Biological

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ABSTRACT

Laser ablation and biosynthesis are two promising and sustainable processes for obtaining nanoparticles (NPs). This work focused on these two methods among the many nanosynthesis methods because they are easy and environmentally friendly. These two methods were used to synthesize cobalt nanoparticles (CoNPs), which were then characterized optically and structurally. The results showed that the obtained CoNPs had a hexagonal phase and polycrystalline structure with the average crystalline size of (27.21 nm) and (76.83 nm) when synthesized physically and biologically, respectively. The resulting NPs' shapes were semi-spherical with the appearance of elliptical shapes due to agglomeration. The biologically synthesized NPs were more absorbent compared to the physically synthesized ones, as the biological method produced a higher concentration of NPs. This work discusses one aspect of the simple comparison between the two sustainable syntheses, with a proposal for its future development.

Keyword / Bottom-up, CoNPs, laser ablation, sustainable methods, top-down

1- Introduction

Nanoscale materials have wide-ranging applications in various fields of life [1-3]. This multiplicity of applications and their fields is due to the fact that NPs have the ability to enhance and improve various properties of materials in an interesting way. Controlling the composition, properties, and structure of NPs allows for a very wide range of applications, leading to significant technological advances [4]. Among the most important parameters that affect the properties of NPs are their size, shape, and structure [5, 6]. To control these parameters, the methods of synthesizing NPs have been varied. These methods may have a physical basis, another group has a chemical basis, and another group has a biological basis. All of these methods fall into one of two main categories: the top-down approach and the bottom-up approach. The starting materials for top-down methods are raw materials, such as pure metals, which are converted into NPs using this approach [7]. While the raw materials for the bottom-up methods are atoms or molecules [8], Figure (1) illustrates both approaches [9].

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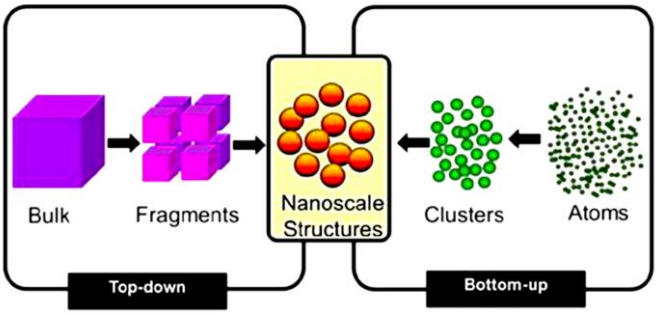


Fig. 1: Top-down and bottom-up synthesis of nanofabrication [9]

One of the top-down approaches is pulsed laser ablation in liquid (PLAL), which can produce pure and highly reactive NPs [10, 11]. This technique generates NPs with interesting properties, which may have stable or unstable structures, simple or complex, etc., making them suitable for many applications [12]. Based on the raw materials, conditions, and waste generated from various laboratory processes, it is considered environmentally sustainable, easy, and economical [13]. As mentioned, the size and shape of the resulting NPs have a direct impact on their properties, so a major focus of future research will be to understand how to control these parameters [10]. This process occurs when the surface of the target solid material, placed in a liquid medium, interacts with the laser beam, which leads to the removal of nanoscale particles from this surface. A colloidal solution of this material is formed, containing the removed NPs [14, 15]. One of the bottom-up approaches to NPs synthesis is biosynthesis (green synthesis), a sustainable and environmentally friendly method that involves reducing metal salts used as raw materials by certain plant species that contain bioactive chemicals. Reducing agents can be based on microorganisms such as bacteria and fungi [10]. Flavonoids, phenols, ketones, aldehydes, amino acids, and vitamins present in the chemical composition of plants have a high capacity to reduce various metal ions [16]. These two sustainable methods can be used to synthesize NPs of different metals, such as cobalt (Co), which is of interest to researchers due to its multiple potential applications in various fields [17]. This work aims to synthesize cobalt nanoparticles (CoNPs) using two sustainable methods: physical and biological methods, PLAL, and the green method using plants, respectively, and then characterize the resulting NPs based on some parameters to determine their importance in choosing the appropriate method for potential applications.

2- Materials and methods

CoNPs were synthesized using two techniques: the first one involved PLAL, using a pure cobalt sheet of dimensions (1 cm × 1 cm × 2 mm) immersed in a beaker of (3 mL) of deionized water (DW). After immersion, the height of DW above the sample was (5 mm). The sample was subjected to a number of pulses (500 pulses) of a Nd: YAG laser at a pulse energy of (100 mJ), a pulse duration of (9 ns), a repetition rate of (5 Hz), and a wavelength of (532 nm). This technical process took less than (2 min).

The second one is a biological approach using saffron (Crocus sativus) plant extract as a reducing agent for cobalt chloride. The plant extract was prepared by dissolving (0.5 g) of the plant in (20 mL) of DW, heating by using a magnetic stirrer at a temperature not exceeding (80 °C) for (6 min), and then filtering the resulting solution. A solution of (1 M) of cobalt chloride was then prepared by dissolving (0.2379 g) of aqueous cobalt chloride in (50 mL) of DW, heating by using a magnetic stirrer at (50 °C) for (15 min). Finally, (5 mL) of the plant extract solution was added dropwise to the cobalt chloride solution. Then the structural properties of the NPs synthesized in the two solutions were determined using X-ray diffraction (XRD) and transmission electron microscopy (TEM), while the optical properties were determined using the UV-visible spectrophotometer (UV-Vis) techniques.

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3- Results and Discussion

The XRD results of the two prepared samples show the formation of hexagonal polycrystalline phases of CoNPs with varying degrees of crystallization and prevailing orientations, as in Figures (2) and (3) for the samples prepared at physical and biological conditions, respectively. Table (1) shows their interatomic distances (d), the full width at half maximum of the diffraction peaks (β), and their average crystal size (D) which had calculated from Equation (1), Debye-Scherrer [18], which represents the, where D equals (27.21 nm) for the CoNPs synthesized physically, it is smaller than the those synthesized biologically, which equals (76.83 nm).

$$D = \frac{0.9\,\lambda}{\beta\cos(\theta)} \quad \ldots\ldots (1)$$

Where λ represents the wavelength of X-rays. The differences of the average crystalline sizes are due to the nature, as well as conditions of the two synthesis technique used, starting from the raw materials used in the synthesis to the temperature and time taken, as they affect the nucleation, crystallinity, and, as a results, crystal sizes. Table (1) also shows the Miller indices (hkl) corresponding to the angles of diffraction, which match JCPDS (card no. 96-901-2885).

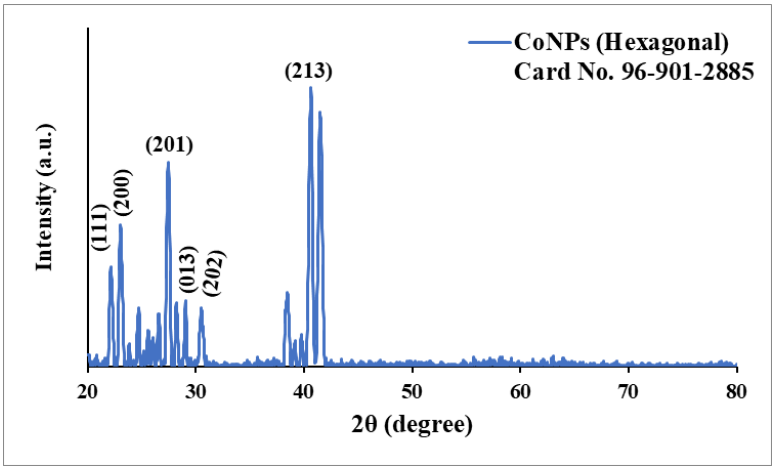


Fig. 2: XRD pattern of CoNPs synthesized physically

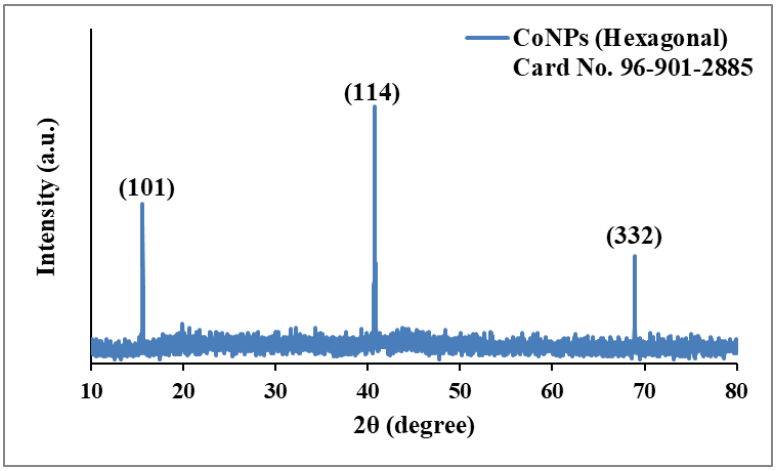


Fig. 3: XRD pattern of CoNPs synthesized by biologically

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Table 1: XRD data of CoNPs synthesized by physical and biological methods

Method	2θ (deg)	hkl	β (deg)	d (nm)	D (nm)
Physical	22.13	111	0.35	0.4012	23.1189
	23.01	200	0.4	0.386	20.26
	27.41	201	0.4	0.325	20.4348
	29.03	013	0.15	0.3072	54.6867
	30.45	202	0.4	0.2932	20.5751
	40.61	213	0.35	0.2218	24.1924
Biological	15.57	101	0.2	0.5684	40.0753
	40.73	114	0.09	0.2212	94.1183
	68.94	332	0.1	0.136	96.3243

Figures (4) and (5) show the formation of agglomeration and clustering in the TEM results for CoNPs synthesized by physical and biological methods, respectively. Both methods produce semi-spherical CoNPs that often appear more elliptical due to clustering and agglomeration. Strong chemical bonds and high surface energy cause increased agglomeration and clustering [19]. The average sizes observed are (30 nm) for the physical method and (35 nm) for the biological method. Although the volume averages are small, agglomeration may delay effectiveness in potential biomedical applications.

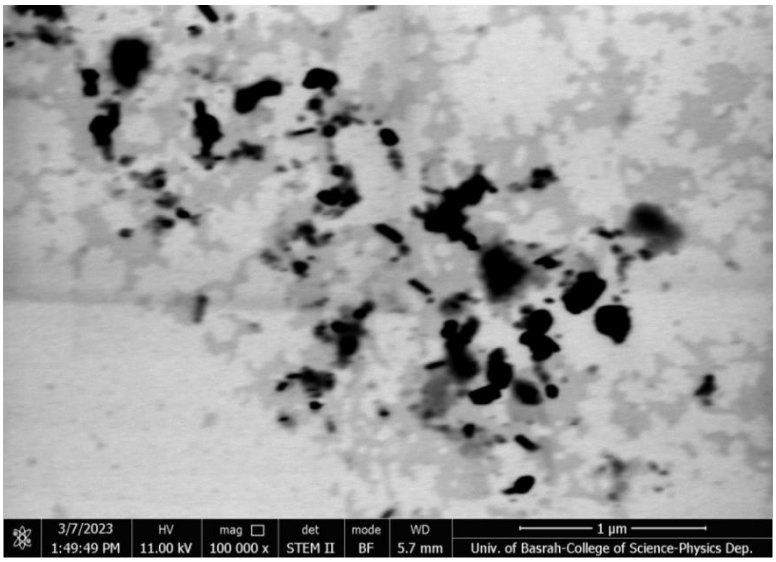


Fig. 4: TEM image of CoNPs synthesized by physical method

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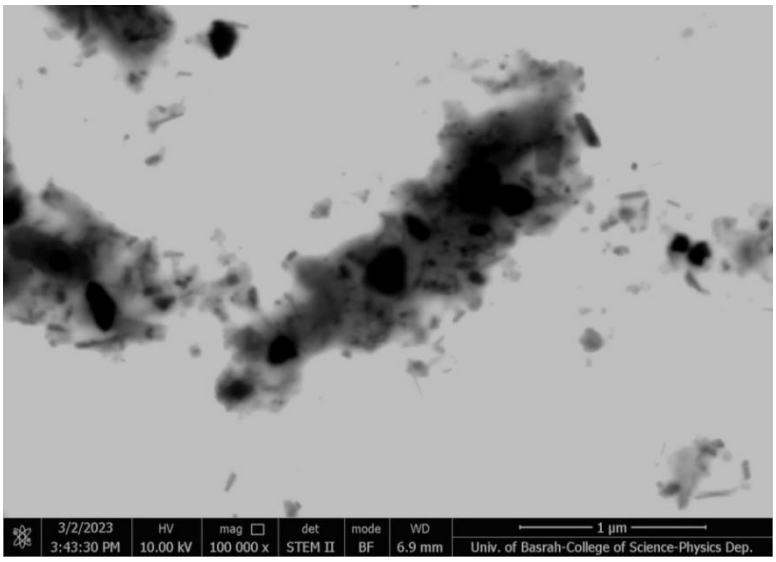


Fig. 5: TEM image of CoNPs synthesized by biological method

Absorbance and absorption coefficient represent the most important optical properties of NPs in general. Figures (6) and (7) show the spectra of these two properties, respectively, which result from UV-Vis analysis of CoNPs synthesized using the two methods. The absorbance spectrum of the biologically synthesized CoNPs is higher than that of the physically synthesized ones. This is due to the high concentration of CoNPs in their biologically prepared colloidal solution, and this confirms the high effectiveness. The physically synthesized CoNPs have a more regular absorption spectrum, as a result of the stability of these NPs in their colloidal solution. This result is consistent with what was observed from the structural characterization results in terms of the average sizes of the resulting nanoparticles as well as the average crystal sizes. The increase and widening of the absorption peak and its shift towards higher wavelengths (red-shift) results from an increase in the size ratio for these biologically synthesized nanoparticles. From equation (2) [20], the absorption coefficient (α) of CoNPs was determined, which was represented as a function of photon energy. The equation shows that its values depend on the absorbance (A) values. The absorption coefficient determines the light transmittance through a path (t) within the material before its absorption, so the high concentration compared to the biologically prepared NPs led to them having a higher α than those prepared physically.

$$\alpha = \frac{2.303\ A}{t} \qquad \dots (2)$$

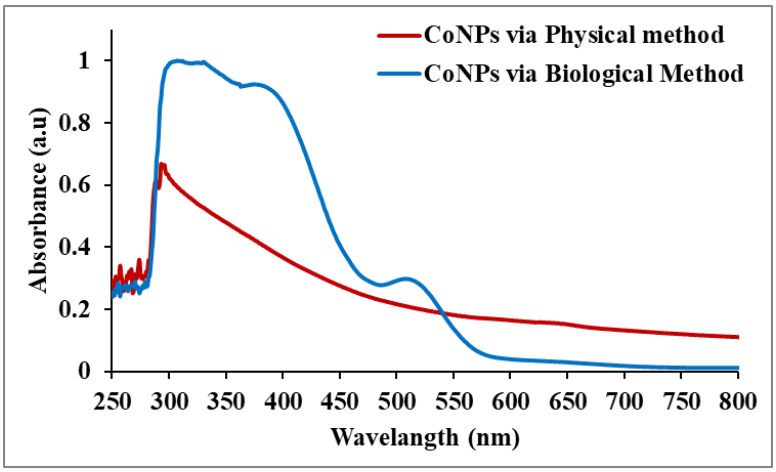


Fig. 6: Absorbance spectra of CoNPs synthesized by physical and biological methods

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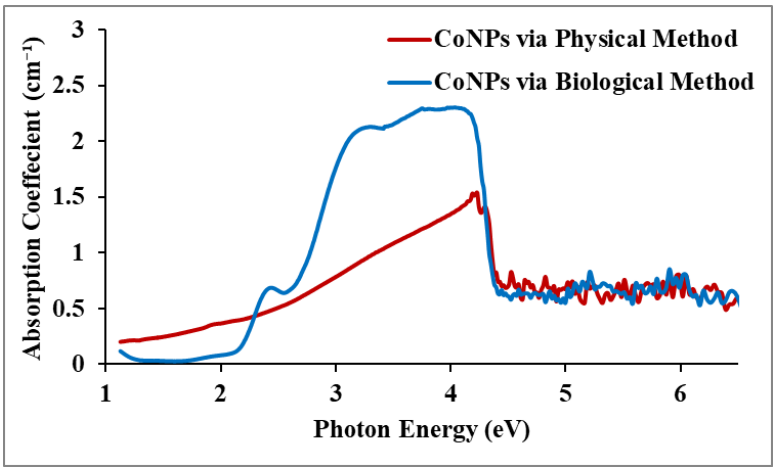


Fig. 7: Absorption coefficient of CoNPs synthesized by physical and biological methods

These results demonstrate that the properties of the nanoparticles produced by the two methods vary depending on the preparation conditions and materials used. These results can be improved by changing different preparation parameters and by conducting in-depth characterization using additional techniques to achieve optimal characterization. Numerous recent studies have revealed a great diversity in the potential applications of the resulting nanoparticles, based on the characterization of the resulting nanoparticles. In this context, researchers in [4] presented a set of significance criteria that researchers must benefit from in choosing different nanosynthesis techniques according to the required application and taking into account environmental sustainability through a simplified description of the first letters of the word (significance) as follows: (s) selection of analysis by direct technique, (i) integration of operational and analytical processes, (g) generation of as little waste as possible, space and treatment, (n) never waste of energy as little as possible, (i) implementation of automation and simplification of methods, (f) favor of factors that can be obtained from a renewable source to preserve health and the environment, (i) increased safety of workers by choosing a simplified and safe technique, (c) conducting on-site measurements, (a) avoiding derivatives and accidental results that may be harmful, (n) note that the size and number of samples should be as low as possible, (c) choose of multi-analytical methods to suit different conditions and with multiple parameters, and (e) elimination or replacement of harmful reagents.

4- Conclusion

Both laser ablation in liquid media and the biological method using plants are promising and sustainable methods for the future of obtaining colloidal solutions of NPs. By comparing the properties of the resulting NPs, comparing the two methods in terms of the raw materials used in preparation, their quantities, and the time required, under current working conditions, it can be said that the physical method is less expensive, except for the cost of the laser device used. It is currently easy to obtain ablation equipment with good specifications and operate it many times and for long periods. The time and effort required to prepare samples using laser ablation are also less. By characterizing the resulting NPs, specifically using optical characterization, it was found that the current working conditions produced a higher concentration of NPs synthesized by the biological method compared to those obtained by the ablation method. As for the structural characterization, it shows a similarity in the shapes and formation of the agglomerates of the NPs synthesized by the two methods, noting that their size ratios are lower than those synthesized physically. This diversity in characterization is useful in choosing the appropriate technology for the required application in all fields. The results of this work can be improved by using different materials and

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preparation parameters in both methods to achieve control over the resulting properties and suitability for different applications. Both methods can also be combined to synthesize NPs with excellent specifications.

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Author contribution: Authors contributed equally in the study.

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