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GREEN SYNTHESIS OF COBALT NANOPATRICLES BY USING ULTRASOUND WAVES, WALNUT GREEN SKIN EXTRACT AS REDUCING AGENT AND EVALUATION OF PHOTOCATALYTIC ACTIVITY

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ABSTRACT

In this investigation, one-step synthesis of cobalt nanoparticles using aqueous extract of walnut green skin with the help of ultrasound waves and photo-catalytic activity as reducing agents was investigated and researched. After conducting preliminary tests and obtaining nanoparticles, The resulting particles were analysed using a scanning electron microscope (SEM) and the size of the particles was between 22 - 70 nm, then X-ray diffraction (XRD) analysis of the average size Cobalt crystals was shown to be 549 nm by Fourier transform infrared spectroscopy (FT-IR) of the sample was studied and the functional groups, OH, CH, C=C and CO, which indicated cobalt metal, were observed. After that, the photo-catalytic activity of cobalt particles on methylene blue was tested and studied, and the degree of its degradation was checked using ultraviolet-visible spectrometry (UV-Vis). SEM determines the structure of nanoparticles. Also in this study, ultrasound waves were used, and the sound waves hit the molecules of the extract and cause more vibrations. These vibrations cause the intrinsic activities of the molecule, because of which the formation of suitable bonds happens earlier and better.

Keywords: cobalt nanoparticles; green synthesis, photocatalytic activity, ultrasound, walnut.

INTRODUCTION

In nanoscience and nanotechnology, tiny science. have been studied, and used in many scientific fields, including engineering, material science, chemistry, physics, and biology [1]. Nanotechnology examines particles with a size of 1 to 100 nm and 3D structure and is based on nanoparticles. These materials are accessible in different shapes and sizes, for example, rod forms, needles, spherical, and crystal [1]. Various chemical, physical, and biological methods are applied to produce nanoparticles. Use of physical processes requires high price, temperature, and pressure. Also, most chemicals are used to perform chemical methods that are hazardous and toxic to biological and environmental systems. Production of contaminated products is another problem of using chemical methods [2]. Thus, there is need to discover a cheap, toxic-free, and highly efficient method. One of the other methods is the biological method that is used to produce nanoparticles [2]. There is a considerable list of sources including plants and plant extracts for the biological production of metal nanoparticles [3]. Lately, many plants can be used to synthesize nanoparticles. Generally, the photosynthesis of nanoparticles obtained from plants has numerous benefits. Water is a safe solvent used in the photosynthesis of nanoparticles prepared from plant extracts [4]. The biosynthesis of nanoparticles obtained from plant extracts does not require special conditions that are necessary for chemical and physical methods, and this method is also straightforward. Plant extracts need less time to form nanoparticles, so these plant extracts have more significant reduction potential than the microbial culture medium [5]. The pollution caused by the biosynthesis of nanoparticles from plant extracts is about zero and less than another method. Hence, the biosynthesis of nanoparticles from plant extracts is more compatible with the environment [6]. The production quality, speed, and other specifications of the nanoparticles produced from plant extracts depend on some factors, for example, time, temperature, pH, salt concentration, the concentration of extract and nature of plant extract [7]. Some phenolic compounds have redox activity include phenolic acids, flavonoids, and tannins. They are crucial to reducing vegetables, fruits, and medicinal plants or antioxidant activity. Compounds of phenolic behave like metal chelating agents, singlet oxygen quenchers, reducing agents, and hydrogen donators, owing to their redox activities [8]. There are different types of phenolic compounds in plant extracts. They are involved in redox reactions and are very reactive. The reduction and creation of metal nanoparticles are the reason for the presence of phenolic substances in plant extracts [9]. Numerous compounds in plant extracts play the primary role in the capping agents, precursor salts reduction, and metal ions absorption mechanism [10]. Walnut skin extract is green, safe, eco-friendly, and interesting to herbalists and pharmacists. Walnut skin extract has medicinal properties such as antiphrasic, antiviral, antibacterial and fungicidal. Its fungicidal properties are due to the presence of Jugolden in it. Also, walnut skin can be used to treat candida, yeast, and infections of ringworm [11 - 14]. Thus, there are 32 various phenolic compounds in the pyrrolegneous acid of walnut skin, which include 4-hydroxy-3,5-dimethoxy-benzaldehyde, 1,2-benzenediol, 1-(4-hydroxy-3,5-dimethoxyphenyl) ethanone, 1- (4-hydroxy-3-methoxyphenyl)-2-propanone, 2-Methoxy-phenol, 3-methoxy-1,2-benzenediol, 2,6- dimethoxy-phenol, 4-ethyl-2-methoxy-phenol, 4-methylphenol, 2-methoxy-5-methylphenol, and phenol are the essential phenolic compounds [15 - 17]. In recent studies on the synthesis of Co NPs using plant extracts containing *Vitis rotundifolia* [28], *Aspalathus linearis* [29], *Taraxacum officinale* [30], *Celosia argentea* [31], and *Sageretia thea* [32] and the leaf extract of *Muntingia calabura* [33]. Cobalt nanoparticles (CoNPs), due to their abundance, cheapness, and versatility, have been developed and investigated. CONPs can have variable spin states bound to oxygen because they have suitable band gaps and multivalent oxidation states. In addition, they have unique magnetic, electrical, and catalytic properties[18], and make a good substitute for noble metal nanoparticles. CoNPs are more stable at neutral pH levels and show photo-catalytic properties in visible light [19].They are good candidates for dye degradation. CoNPs or their composites are used to degrade some dyes, including acid blue 74 [20], Congo red [21], methyl orange, direct yellow-142 [22], methylene blue (MB), Erythrosine B [23]. The purpose of this study is (i) Synthesis of CoNPs using walnut skin extract, checking their chemical, optical, and structural properties using different methods, and (ii) Their photo-catalytic potential for the degradation of methylene blue (MB) dye has been investigated.

EXPERIMENTAL

Synthesis and procedures

Preparation of walnut green skin extract

Some walnut green skin is prepared after drying in a suitable environment. It is washed once with city water and several times with deionized water to remove external pollution or dust. In the next step, 20 g of the plant was mixed with 90 mL of deionized water and placed on the heater with a temperature of 60 - 80°C for 5 min to obtain the plant extract. In this step, a dark brown solution is obtained. Then, the resulting mixture is passed through a mesh cloth to separate the large pieces of walnut skin. Next, the mixture was passed through filter paper for further filtration.

Synthesis of Co NPs

90 mL of deionized water was added to 300 mg of cobalt nitrate and placed in the ultrasonic device for 14 min. Then, NaOH solution is added dropwise to the reaction mixture to make pH = 14. Then, the solution was placed on the heater for some time to allow the material to settle. After that, the sediment was separated from the extract inside the Erlenmeyer, and the material was rested for a week. Then, it was placed in a centrifuge at 1400 round per minute for 20 min. The supernatant mixture was discarded, and in the process of centrifugation, the sediments were washed once with water until the remaining extract and once with alcohol to remove other organic compounds and dried. The remaining water in the nanoparticle mixture was cleaned and rested for a second time for one day. Finally, cobalt nanoparticles were collected for analysis after drying.

Photo-catalytic degradation of MB dye by CoNPs

Different amounts of powdered nanoparticles were dispersed, 10 mg of methylene blue was added to deionized water, and the solution was rested in the dark for about 2 h. Then, the number of NPs weighed with methylene blue solution was increased to 25 mL and placed on the heater, and the catalytic amount of nanoparticles was studied.

RESULTS AND DISCUSSION

Characterization of Co NPs

UV-Vis is a chemical analysis method that used to identify and qualitatively analyse chemical products. The suitable wavelength for UV-Vis is between 200-800 nm. The electrons of molecules or atoms are excited under UV-Vis radiation and move from low-energy to high-energy levels [24]. As seen in Fig. 1, the spectral information has peaks at 212 nm, 325 nm, and 434 nm, indicating cobalt nanoparticles.

XRD was performed to study the crystal plane, size, and structure of CoNPs. Narrow and intense diffraction peaks showed the suitable crystalline nature of the synthesized CoNPs [25]. The size of these nanoparticles was measured based on the broadening diffraction peaks corresponding to the most critical reflections. Furthermore, the Debye-Scherrer equation was used to analyse the size of the crystals.

FT-IR is used to analyse transitions and vibrations in molecules at vibrational and rotational levels by collecting high-resolution data over a broad spectrum. As a function of electromagnetic radiation interference, this method helps provide data on different functional groups on the surface of a nanomaterial. Fig. 3 shows the FT-IR results in the range of 400 - 4000 cm^{-1} of the obtained extract. By carefully observing the infrared spectrum of walnut green skin nanoparticles, a broad peak at 3525 cm^{-1} represents an OH stretch bond and indicates the presence of an alcohol functional group in the substance. Two short peaks at 2817 cm^{-1} and 2849 cm^{-1} indicate two C-H stretching bonds, which confirms the existence of two alkane functional groups. The next peak at 1610 cm^{-1} shows a C=C stretching bond, which is an unsaturated ketone. The peak at 1385 cm^{-1} shows that the C-H bending bond is an aldehyde. It shows the first type of alcohol, and the last peak can be attributed to CO, which indicates the formation of cobalt nanoparticles.

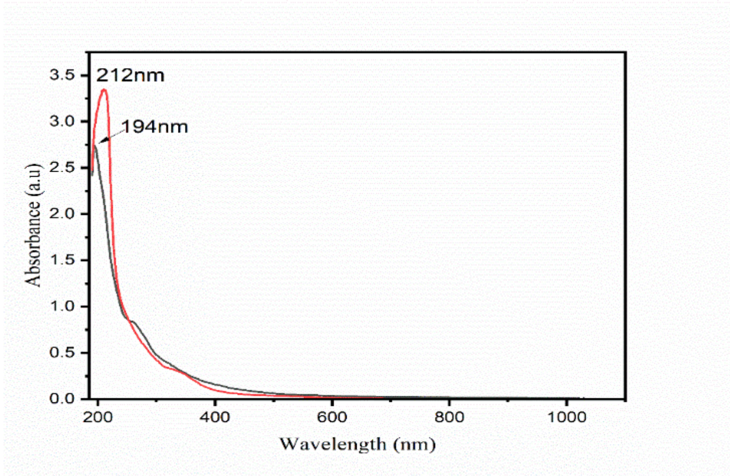

Fig. 1. UV-Vis spectra of CoNPs.

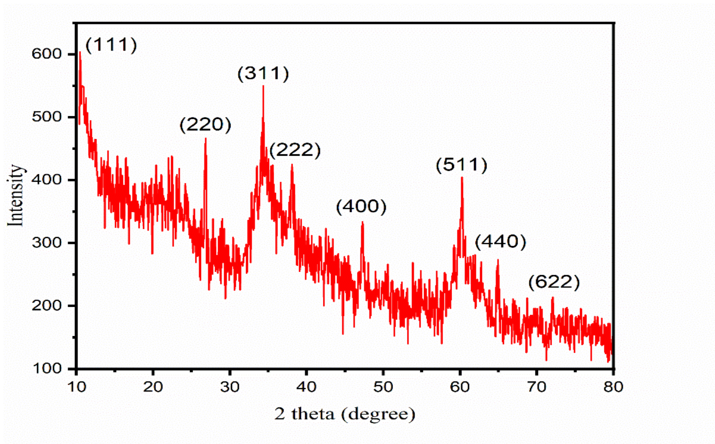

Fig. 2. XRD pattern of Co NPs.

The output images from SEM are produced using electrons and have many applications in materials science and nanotechnology [26]. This technique helps study various specimens. The SEM image of Co NPs, The SEM image of Co NPs, which shows the particle size between 22 - 70 nm, proves the synthesis of nanoparticles.

Photo-catalytic activity

Photo-catalytic degradation of MB was investigated using synthesized Co nanoparticles under visible light irradiation. While the 3d orbital contributes Co^{2+} carriers in the conduction band. The valance band is determined by the (2p) orbital having O^{2-} carriers. Because the charge is transferred (O^{2-} to Co^{2+}). When the photons were illuminated, the photo-catalytic degradation process was enhanced because a reaction was carried out

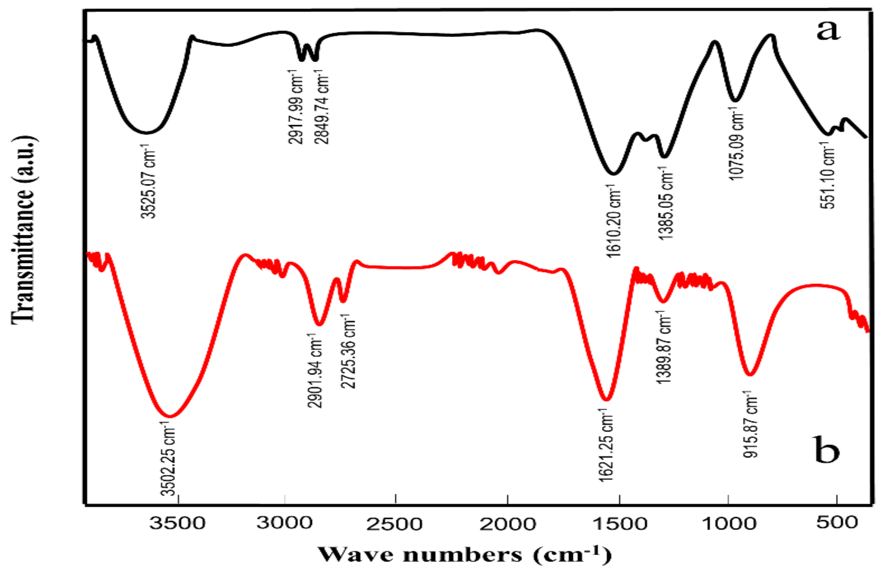

Fig. 3. FT-IR spectra walnut green skin extract.

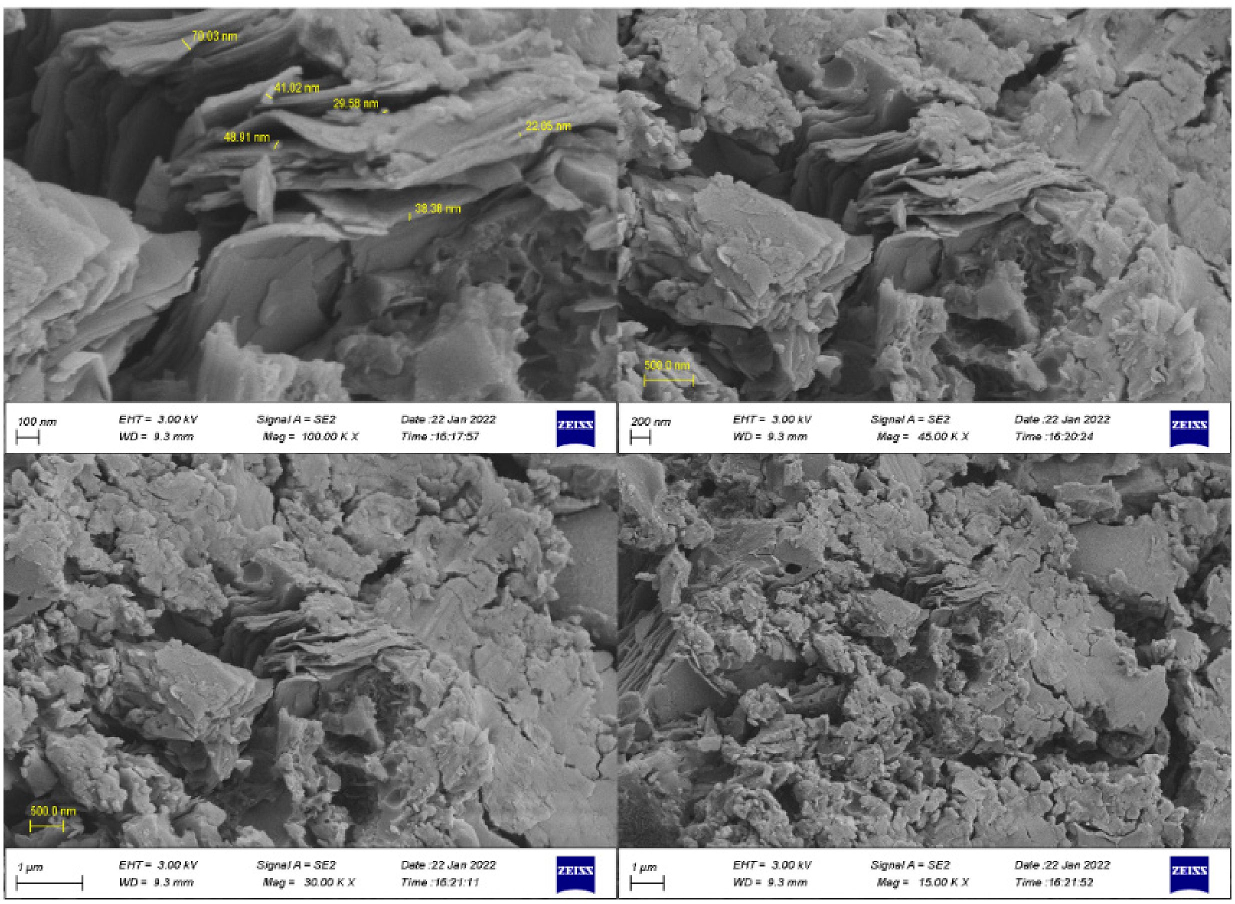

Fig. 4. SEM analysis of Co NPs.

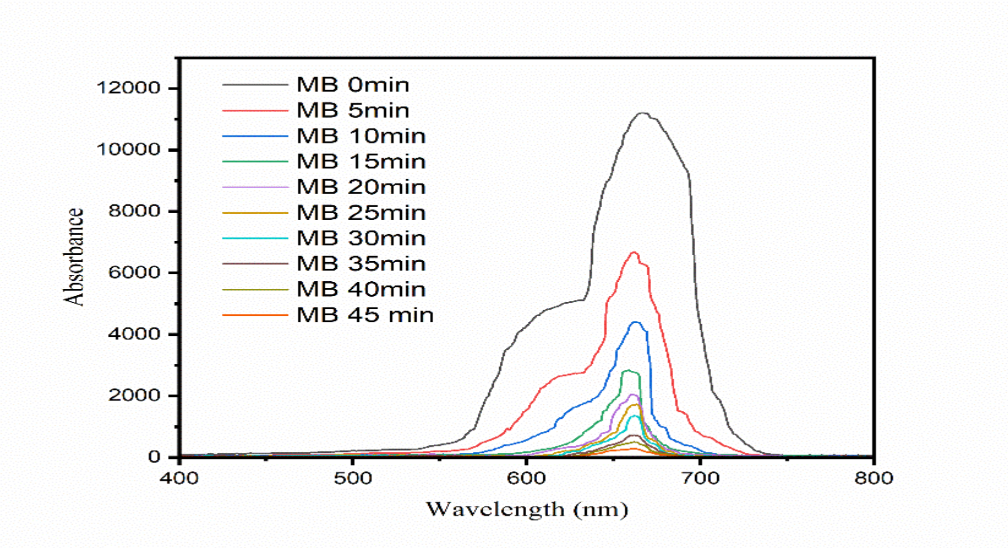

Fig. 5. Photocatalytic diagram with 80 mg concentration at different times.

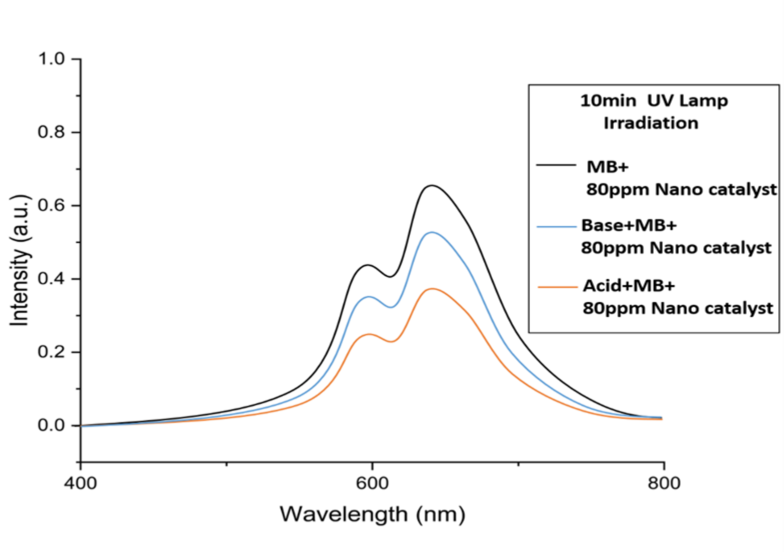

Fig. 6. Effect of the solution pH on the photo-degradation of MB dye.

by the methylene blue dye, introducing electrons into the lattice plane of the Co nanoparticles and generating superoxide radicals in the presence of oxygen in the solution. The photo-catalytic degradation of the target dye is associated with the removal of the chromophoric group and the conversion of the dye into low molecular weight side-products [27]. Under the conditions of irradiation of visible light, the formation of holes (h+) and electrons (e-) on the surface of the catalyst causes colour degradation. For the construction of OH radical, water molecules mix with h^+ holes, and then the O_2 molecule converts to OH through HOO and H_2O_2 intermediates. OH is a strong oxidizing agent and the colour of organic molecules is non-selectively decomposed by OH into CO_2, H_2O, and mineral ions [28]. Fig. 5 shows different concentrations of nanoparticles in methylene blue during 10 minutes under UV light. The first peak of methylene blue is without nanoparticles and the concentrations are 5, 10, 15, 20, 25, 30, 50, 60, and 80, respectively, which is the last peak that has the highest efficiency. 80 mg of nanoparticles were exposed to UV radiation for 10 minutes, which destroyed a significant amount of methylene blue.

Effect of pH

The effect of the solution pH on the photo-degradation of MB dye was investigated in the range of 5 - 11 for 10 min at room temperature. The concentration of 80 mg of nanoparticles is under UV radiation for 10 min (orange diagram). The blue diagram is 80 mg of nanoparticles plus acid (pH < 7) under UV light irradiation, which has good efficiency and has catalyzed methylene blue. The last diagram is a green diagram, 80 mg of nanoparticles to which base (pH > 7) was added and exposed to UV light for 10 min, which is the highest efficiency related to this chart and has the highest percentage of methylene blue destruction.

CONCLUSIONS

Recent studies have shown a clean, useful and eco-friendly method for synthesizing cobalt nanoparticles using green walnut skin extract. The biosynthesis method does not have the problems that exist in the physical and chemical methods for synthesizing nanoparticles, and it is an easy, cheap, and non-toxic method. The synthesized CoNPs were analysed using UV-Vis, FT-IR, XRD, and SEM. In UV-Vis, the presence of cobalt nanoparticles was confirmed with a strong absorption peak at 212 nm. Alcohol functional groups were confirmed by FT-IR analysis and synthesized CoNPs were found as pure crystals by XRD test. The morphology of the synthesized CoNPs is spherical, which is characterized by the SEM device. Also, for the Photo-degradation of MB colour, Co nanoparticles are used as a photo-catalyst.

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