Green Synthesis of Cobalt Nanoparticles and their Application in Removal of Lead from Polluted Water

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Doi:10.29072/basjs.202129

Abstract

Cobalt nanoparticles were synthesized by reduction-oxidation method. The reaction was done using cobalt salts as the source of metal and eucalyptus leaf as a reducing material and trisodium citrate used as capping agent. The creation of the cobalt nanoparticles was monitored using UV-Vis spectroscopy. The UV-Vis spectroscopy shown the formation of cobalt nanoparticles by exhibing the typical surface plasmon absorption maximum at 570 nm. Fourier transform infrared spectra (FTIR) used for characterization of eucalyptus leaf some functional groups that related with cobalt nanoparticles was showed. Field emission scanning electron microscope (FESEM) was monitored to characterize the morphology and the size of cobalt nanoparticles, images from FESEM indicate that the synthesis of cobalt nanoparticles in the range (15-85 nm). Dynamic light scattering (DLS), by zeta sizer analysis showed the distribution of nanoparticles in nano range; moreover, zeta potential analysis clarified the distribution of cobalt nanoparticles in a negative value (-20.3mV), which indicate presence of stable and positive cobalt ions. The production of cobalt nanoparticles were applied for removal of heavy metals from polluted water and flame atomic absorption spectroscopy (FAAS) was used for determination of polluted metals before and after the addition of nano cobalt.

Article inf.

Received: *14/7/2021*

Accepted: *29/8/2021*

Published: *31/8/2021*

keywords:

Cobalt nanoparticles, Eucalyptus leaves extract, removal of lead, Atomic absorption spectroscopy

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1. Introduction

Nanoparticles are a crucial field of recent research handling design synthesis, manipulation of particle structure starting from about (1-100) nm [1]. Nanoparticles are often synthesized by physical, chemical or biological methods [2]. Metal nanoparticles are used broadly in several fields using bio field, catalysis and photonics [3]. Cobalt nanoparticles are often synthesized via many techniques like, spray pyrolysis, ultrasound device, Dc magnetron, and sputtering coating [4], warm structure [5], decomposition by heating [6], electrochemical [7] and liquid-phase reduction [8] and as well by biological methods like microbial synthesis [9] of nanoparticles. Cobalt nanoparticles could be efficient nanoparticles as they have good catalytic activity [10,11] and high performance stable magnetic properties [12,13] and also have biomedical properties [14] and cytotoxic activity[15]. Green synthesized nanoparticles have gained importance [16] due to their use of a variety of reducing agents including; cow's milk, microbes, [17]. Recently, several approaches are achieved for the synthesis of nanoparticles using the plant extract. These procedures have acquired significance because of their properties, as simplicity and, cost effectiveness [18]. The adsorption concept by nanoparticles is new, many types of adsorbent such nanoparticles were used for removal of heavy metals [19]. Green chemistry notion was taken into consideration when synthesizing cobalt nanoparticles using eucalyptus leaves. The aim of this study was to evaluate the purification of water from heavy metals.

2. Materials and methods

2.1 Preparation of Aqueous Plant Extract

Eucalyptus is an evergreen tree widely used for its medicinal properties as it is used to relieve symptoms of coughs colds and choking. Leaves eucalyptus globus was collected from the gardens of Al-burjisiya in west Basra-Iraq. The sliced leaves washed with deionized water, then dried by air at room temperature 25°C for about 12 days and crushed to a fine powder. Then 10 gram of leaves powder are taken and dissolved in 200 ml of deionized water, after that the solution was shacked at 35°C for 6 hours. The solution was filtered through filter paper (Whatman- 1), and the filtrate was used immediately for the production of cobalt nanoparticles.

2.2 Synthesis of cobalt nanoparticles

For the synthesis of cobalt nanoparticles, 50 ml of the aqueous leaves extract was added to 450 ml of (1×10^{-3} M) from ($CoCl_2$. $6H_2O$) solution and stirred for about 30 min. During the stirring of (0.1g) of trisodium citrate was adding as a masking agents, after 48 hours the changing

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in color was detected from brown to light brown color, indicating for the synthesis of cobalt nanoparticles as can be seen in Fig. 1.

Figure 1: The stages of changing color of cobalt nanoparticles.

2.3 Preparation of pb (II) stock solution

A series of standard solutions of lead (II) were prepared using standard solution at a concentration of (1000 mg. l^{-1}) with deionized water.

2.4 Study of Adsorption

Batch equilibrium experiments had been carry out to find the optimum conditions for equilibrium isotherms. A series of (100 ml) covered conical flasks were used addition of 15ml of cobalt nanoparticles to 15 ml of (10 mg. l^{-1}) of metal was done. The experiments were prepared at room temperature, after slight shaking for desired time at 120 rpm then the concentration of lead determines using flame atomic absorption spectroscopy. The removal efficiency and the equilibrium uptake of lead were calculated according to the equations below using (FAAS):

$$\text{Removal } \% = \frac{Co-Ce}{Co} \cdot 100 \qquad \ldots\ldots\ldots 1$$

$$Q_e = \frac{Vsol(Co-Ce)}{m} \qquad \ldots\ldots\ldots 2$$

where C_e is the equilibrium concentration of pb(II) mg. l^{-1}, C_o is the initial concentration of pb (II) mg. l^{-1} , V is solution volume in liter, Q_e is capacity adsorption (mg/g) and m is the mass of adsorbent.

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3. Results and Discussion

3.1 Ultraviolet-visible Spectroscopy (UV-Vis)

Ultraviolet-visible Spectroscopy (UV-Vis) is most widely used to investigation the optical properties of the metal nanoparticles. UV-Visible spectroscopy of synthesized cobalt nanoparticles shows absorption band at 570 nm (Fig .2) this absorption band can be qualified to the surface plasmon of cobalt nanoparticles hence is confirming their formation.

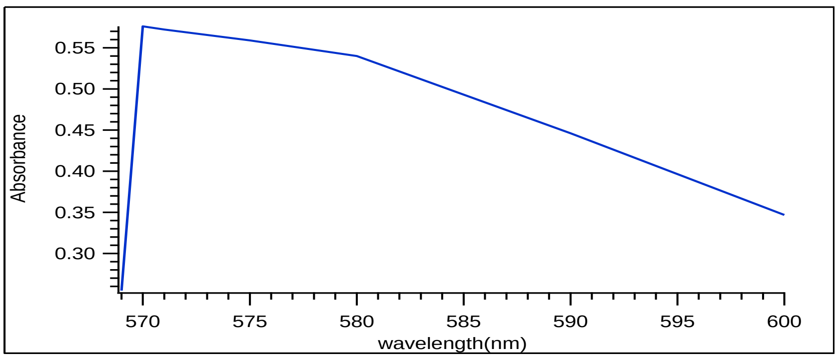

Figure 2 : UV-Visible spectrum of cobalt nanoparticles

3.2 FTIR Analysis

FTIR measurements used to identify the major functional groups on the surface of the plant extract and its possible involvement in the capping and stabilization of the cobalt nanoparticles. In Figure 3, FTIR spectra of cobalt nanoparticles show strong absorption band at 1625 cm^{-1} and it is attributed to binding 3423 cm^{-1} could be due to O-H group in polyphenols or proteins or polysaccharide. FTIR measurements were carried out to detect the possible functioal groups responsible for the cobalt metal nanoparticles . (Table 1) and (Fig 3) display the functioal groups existing in the eucalyptus leaf extract before synthesis and (Table 2) and (Fig 4) show the functioal groups existing in synthesis of cobalt nanoparticles.

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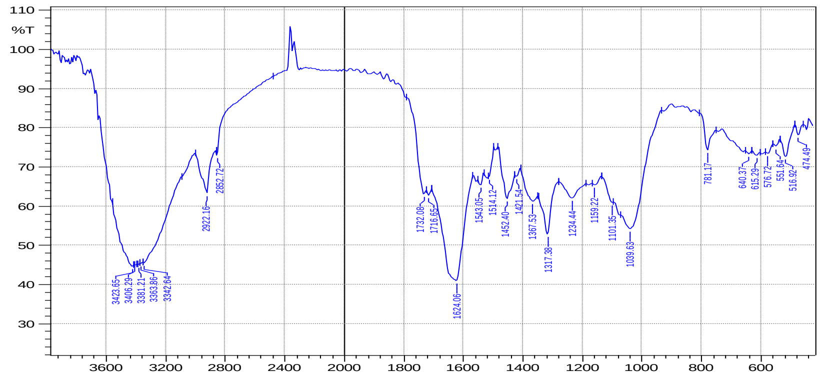

Figure 3: FTIR Spectrum of eucalyptus leaf.

Tab2 1 : Functional groups of eucalyptus leaf.

functional groups	**Peaks**
O-H	3423.65
C-H	2922.16
C=O	1732.08
C=C	1625.99
CH_2	1452.40
C-O-C	1039.63
C-Cl	781.17
C-Br	516.92

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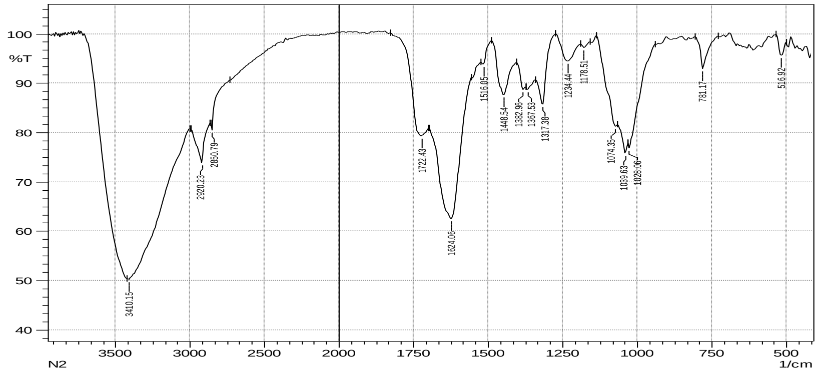

Figure 4: FTIR Spectrum of cobalt nanoparticles.

Table 2 : Functional groups of cobalt nanoparticles

functional groups	Peaks
O-H	3410.15
C-H	2920.23
C=O	1722.43
C=C	1624.06
CH_2	1448.54
C-O-C	1028.06
C-Cl	781.17
C-Br	516.92

By Comparing the FTIR Spectrum of eucalptus leaves and FTIR Spectrum of cobalt nanoparticles it has been observed that the narrow peak at 3410.15 appearing in the spectrum for nanoparticles comparing with leaves extracts. These deferences might be depend on consuming the functional group for reduction of cobalt ion to cobalt nanometal. Some peakes at (640.37 ,615.29,576.72,551.64) appearing in the spectrum of eucalputs leaves did not appear in the

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spectrum of cobalt nanoparticles, this indicates that these functional groups contributed to the reduction of the cobalt ion into cobalt nanoparticles [20]. The plant extract is contain from different chemical materials such phonols which is used for reduction of cobalt into cobalt oxide nanoparticles. However these chemical compounds become passivatted when nano is form [21].

3.3 Field emission scanning electron microscope

Morphology of the surface and both of size and shape of cobalt nanoparticles was identify. It was identified that shapes of cobalt nanoparticles appeared like irregular spherical shape with rough surface (Fig 5). Moreover, the dimension of the particles was in nano range (15-85 nm).

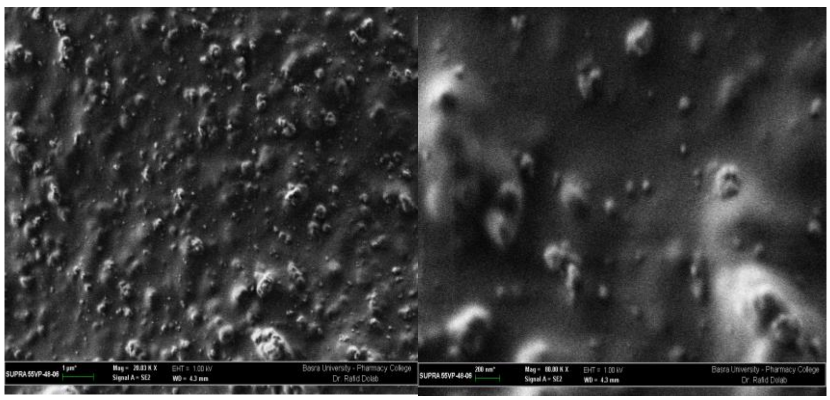

Figure 5: FESEM images of cobalt nanoparticles

3.4 Dynamic light scattering (DLS)

Dynamic light scattering (DLS) is a performance can be used to explain the size distribution of small particles in the suspension. Zeta sizer and zeta potential spectra is a part of (DLS) which can be used to scan the size and the potential of cobalt nanoparticles in the prepared solution. (Fig. 6) shows the distribution of cobalt ion and its clear that the size of nanoparticles almost in the nano range less than 100 nm, however the colloidal is also contain of particles with the size more than 100nm which is result of capping agent from the plant extract . (Fig. 7) Shows the zeta potential distribution of cobalt nanoparticles with good value which is refer to high stability of the solution. In DLS the zeta potential value more than (30 Mv) of nanoparticles indicating for stability of nano colloidal.

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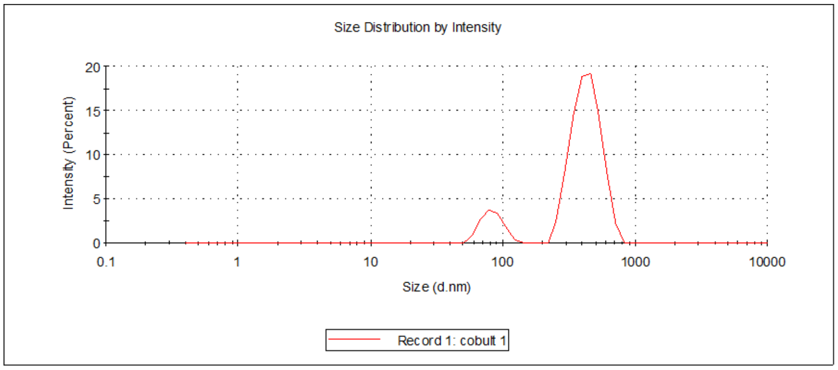

Figure 6: Zeta sizer analysis for synthesized cobalt nanoparticles.

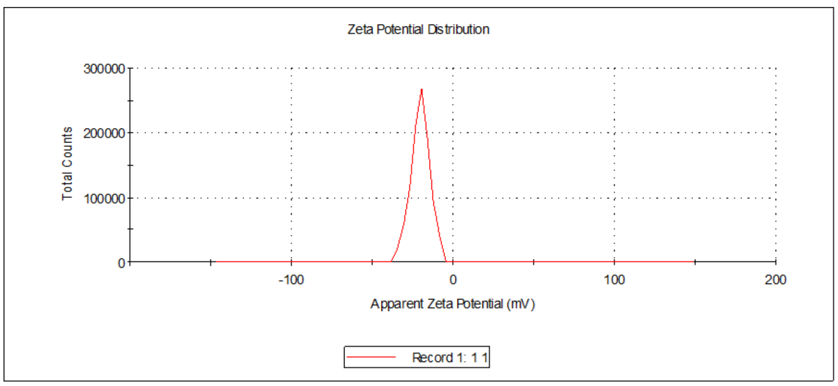

Figure 7: Zeta potential analysis for synthesized cobalt nanoparticles.

4. Applications

Cobalt nanoparticles were applied in the adsorption of lead ion from water using (FAAS), where it showed high efficiency in adsorption. The adsorption was studied by taking two concentrations of pb(II) (5 mg /l) and (10 mg/l) and the removal percentage and the equilibrium uptake of pb(II) ions were calculated depending on the equations 1and 2. Table 3 shows the removal percentage of lead (II) ions were 95% and 92% for (5 mg /l) and (10 mg/l) of lead (II) ions respectively.

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Table3 : Removal ratio and adsorption capacity of pb(II) on cobalt nanoparticles

Pb(Conc. (mg/l))	Removal %	Qe(mg/g)
5	95	7.1
10	92	13.8

The adsorption isotherms were also studied at 25 ° C, and the Langmuir and Freundlich coefficients were. Langmuir (eq.3) and Freundlich (eq.4). Calculated according to the equations:

$C_e/Q_e = C_e/Q_m + C_e/Q_e$ ……….3

Whereas Q_m is the maximum adsorption capacity (mg/g) and b is related to the adsorption energy.

$\text{Log } Q_e = \log K_f + 1/n \log C_e$ …….4

K_f is the Freundlich constant and n is the Freundlich indicator.

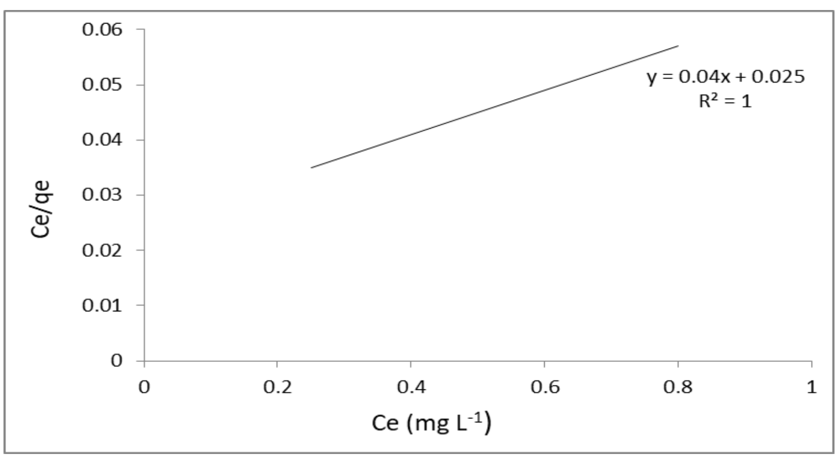

Figure 8: Linear formula of Langmuir isotherm of Pb (II) on Co-nanoparticles at 25°C

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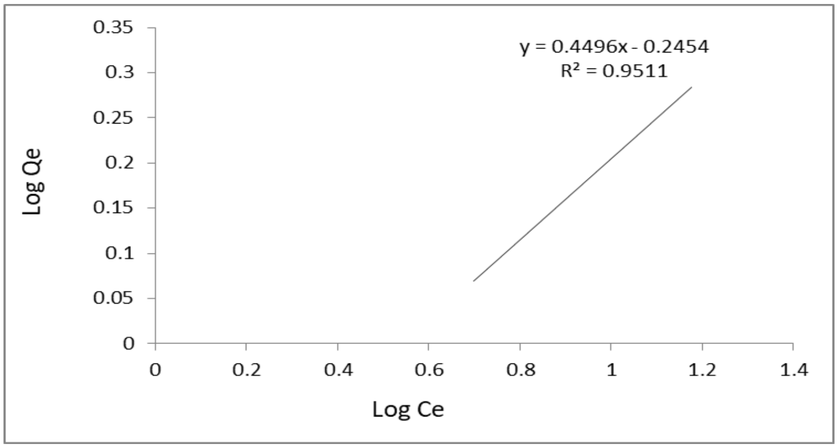

Figure 9: Linear form of Freundlich isotherm of pb(II) adsorbed on cobalt nanoparticles at 25°C

Results obtained from the study of the effect of temperature on the adsorption of Pb (II) on the surface of Cobalt nanoparticles were used in the application of the mathematical equation for Langmuir isotherm for adsorption, Pb (II) draw the linear relationship of the equation as shown in Figure (9) and Table (3) show the values of the amplitude of Langmuir on the surface.

From the isotherms data, the value of the Langmuir constant (b) and the maximum adsorption (Q_m) was calculated. The experimental data have also been applied to the Freundlich equation for adsorption, and the Figure (9) shows the linear relationship of the Freundlich equation for adsorption on the surface of Cobalt nanoparticles and from the data of the isotherms the experimental Freundlich constant was calculated by drawing the linear relationship of this isotherm and calculating the experimental Freundlich constants (n) & K_f. We note through the values of the correlation coefficient that the Langmuir equation is the most applicable to the adsorption of Pb (II) due to the existence of a linear relationship between the values of (C_e/Q_e) versus (C_e). Whereas, the results presented that the Freundlich equation is excluded, as there is no linearity between the Log Q_e and Log C_e values as shown in Table (4).

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Table 4: Langmuir and Freundlich for Pb (II) ions adsorbed on cobalt nanoparticles at 25°C

Pb(II)	Langmuir			Freundlich		
	Q_m(mg/g)	b (l/g)	R^2	K_f	N	R^2
	25	1.6	1	1.73	2.27	0.953

5. Conclusions

A simple, cheap, fast and green method for the preparation of cobalt nanoparticles was achieved. Analysis from SEM shows cobalt nanoparticles in spherical shape. The particle size is in the range (15-85 nm). Zeta potential provide stable solution of nanocobalts. The present work provides a promising method to release heavy metals by cobalt nano product from water. Release percentage about 95% for removing lead ions from polluted water was achieved. Using green chemistry. Hence, this method has less effects on the environment.

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التخليق الأخضر لجسيمات الكوبالت النانوية وتطبيقاتها في إزالة الرصاص من المياه الملوثة

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المستخلص

تم تصنيع جسيمات الكوبالت النانوية بطريقة الاختزال والأكسدة. تم إجراء التفاعل باستخدام أملاح الكوبالت كمصدر للمعدن وأوراق الكينا كمادة مختزلة وسيترات ثلاثي الصوديوم المستخدمة كعامل تغطية. تمت مراقبة تكوين جسيمات الكوبالت النانوية باستخدام التحليل الطيفي للأشعة المرئية وفوق البنفسجية. كشف التحليل الطيفي للأشعة المرئية وفوق البنفسجية عن تكوين جزيئات الكوبالت النانوية من خلال إظهار امتصاص البلازمون السطحي النموذجي بحد أقصى عند 570 نانومتر. تم عرض أطياف فورير لتحويل الأشعة تحت الحمراء (FTIR) المستخدمة في تشخيص أوراق اليوكاليبتوس على بعض المجموعات الوظيفية المرتبطة بجسيمات الكوبالت النانوية. تم استخدام المجهر الإلكتروني لمسح الانبعاث (FESEM) لتشخيص التشكل وحجم جسيمات الكوبالت النانوية ، وتشير الصور من FESEM إلى أن تخليق جسيمات الكوبالت النانوية عند المدى (15-85 نانومتر). أظهر تشتت الضوء الديناميكي (DLS) ، من خلال تحليل حجم زيتا ، توزيع الجسيمات النانوية في نطاق النانو علاوة على ذلك ، أوضح تحليل جهد زيتا توزيع جسيمات الكوبالت النانوية بقيمة سالبة (-20.3 mV) والتي تشير إلى وجود أيونات الكوبالت المستقرة والإيجابية. تم استخدام تركيب جزيئات الكوبالت النانوية لإزالة المعادن الثقيلة من المياه الملوثة ومطياف الامتصاص الذري للهب (FAAS) لتحديد المعادن الملوثة قبل وبعد إضافة الكوبالت النانوي.

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