Chemical Science International Journal

27(1): 1-8, 2019; Article no.CSIJ.48569
ISSN: 2456-706X
(Past name: American Chemical Science Journal, Past ISSN: 2249-0205)

Biological Synthesis of Cobalt Nanoparticles from *Mangifera indica* Leaf Extract and Application by Detection of Manganese (II) Ions Present in Industrial Wastewater

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Authors' contributions

This work was carried out in collaboration among all authors. Author FUO designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Authors HOC and FCO managed the analyses of the study. Author FCO managed the literature searches. All authors read and approved the final manuscript.

Article Information

DOI: 10.9734/CSJI/2019/v27i130106
Editor(s):
(1) Dr. Francisco Marquez-Linares, Department of Chemistry, Nanomaterials Research Group, School of Science and Technology, University of Turabo, USA.
(2) Dr. Yunjin Yao, School of Chemical Engineering, Hefei University of Technology, China.
Reviewers:
(1) Dr. Kartika Rathore, Jai Narain Vyas University, India.
(2) Ekane Peter Etape, University of Buea, Cameroon.
(3) I. Boris Kharisov, Universidad Autónoma de Nuevo León, México.
Complete Peer review History: http://www.sdiarticle3.com/review-history/48569

Original Research Article

Received 16 March 2019
Accepted 01 June 2019
Published 10 June 2019

ABSTRACT

This study was focused on the synthesis of cobalt nanoparticles using *Mangifera indica* leaf extract and the characterization of the particles via UV–Vis spectroscopy, XRD, FT-IR and SEM. The XRD results showed the formation of cobalt nanoparticles that was crystalline in nature, with an average size of 25—40 nm. The FT-IR analysis of the leaf extract reviewed some functional groups responsible for the reduction of cobalt ions to cobalt nanoparticles while the SEM indicates that the synthesised cobalt nanoparticles possess a cubic, pentagonal and irregular in shape with a smooth surface. Application of colloidal cobalt nanoparticles in detecting Mn^{2+} ions was discussed which indicated that the absorption of the Mn (II) ions decreased at increased concentration of Mn (II) ions

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indicating that Mn (II) ion can be detected even at a very low concentration. The minimum and maximum detection limit was found to be 5 and 25 mM of Mn (II) ions, respectively. The obtained results encourage the use of economical synthesis of cobalt nanoparticles in the development of nanosensors to detect the pollutants present in industrial effluents.

Keywords: Mangifera indica; Mn^{2+}; cobalt nanoparticle; industrial wastewater; colourimetric detection.

1. INTRODUCTION

The unique properties of nanoparticles have made nanotechnology the most interesting area of research. The size, shape, and morphology are the crucial parameters deciding the property of nanoparticles [1]. Hence, several studies have been conducted to controlling the size and shape of nanoparticles during the synthesis leading to the method of synthesis, playing a significant role. Although there are many methods of synthesis including chemical and physical methods, these conventional methods of synthesis result in toxic byproducts that are not environmentally friendly therefore there is a need for an alternative method of synthesizing nanoparticles which will not cause environmental hazards. In vitro green synthesis of nanoparticles has gained popularity due to its simplicity, low cost, eco-friendly nature, and easiness to scale-up [2] Ag NPs synthesized using O. sanctum and *Chenopodium aristatum* showed good catalytic activity in degradation of 4-nitrophenol [3,4].

The green synthesized nanoparticles have gained prominence in recent years [5] which uses a variety of reducing agents including; cows milk, plant extract, microbes, and others [6]. Among these methods, the use of green plant extract has acquired a significance due to its properties, such as availability of the source, cost-effectiveness, and others [7]. This prompted interest to synthesize cobalt nanoparticles using an extract from the leaves of *Mangifera indica* and its application in detecting Mn^{2+} from industrial wastewater since no work has been reported on that. *Mangifera indica* is a common flowering evergreen plant that has demonstrated antibiotics properties in vitro and is used in traditional medicine using the extracts of the bark, leaves, stems and unripe fruits [8]. In addition to being eco-friendly, nanoparticles can be synthesized using agricultural and industrial waste to make the process more sustainable [9]. Being cellulosic in nature can be used as an organic surface coating and stabiliser in this approach. In this work, cobalt nanoparticles were biologically synthesized from the solution of cobalt chloride hexahydrate using aqueous leaves extract of *Mangifera indica* as a natural reducing agent. Characterization of the synthesized cobalt nanoparticles was achieved via UV-Visible, FT-IR, SEM and XRD analysis and the colourimetric detection of Mn^{2+} from industrial wastewater were examined using the prepared colloidal cobalt nanoparticles.

2. MATERIALS AND METHODS

2.1 Collection of Plant Materials

The leaves of *Mangifera indica* were collected from Agunachieze village, Okwuohia in Obowo West, Obowo Local Government Area in Imo State, Nigeria. Then, the leaves were taken for identification and authentication at the Taxonomy Section of the Forestry Department of the Michael Okpara University of Agriculture Umudike.

2.2 Preparation of Aqueous Plant Extract

The sliced leaves were washed thoroughly with deionized water, air dried at room temperature for about two weeks and milled to a fine powder. About 25 gramms of the powdered material was dispersed in a 250 mL of deionized water in a 500 mL glass beaker and boiled at 80°C for 15 min and was allowed to cool. After that, the solution was filtered through Whatman No. 1 filter paper (Springfield Mill. Maidstone. Kent, England) and the filtrate was used immediately for the synthesis of cobalt nanoparticles.

2.3 Synthesis of Cobalt Nanoparticles

For the synthesis of cobalt nanoparticles, 100 mL of the aqueous leaves extract was added to 900 mL of 1×10^{-3} M aqueous ($CoCl_2.6H_2O$) solution in a 1000 mL bottle and was stirred for about 30 mins. Within 48 hrs change in colour was observed from reddish brown to dark brown indicating the formation of cobalt nanoparticles. The cobalt nanoparticles solution obtained was purified by repeated centrifugation at 4000 rpm for 15 min followed by re-dispersion of the pellet in deionized water. Then the cobalt nanoparticles were dried in an oven at 80°C and then allowed to cool before storing in an airtight container.

2.4 UV-visible Spectroscopy Analysis

The bio-reduction process of cobalt ions in aqueous solution was measured by sampling 1mL aliquot compared with 1 mL of distilled water used as blank and subsequently measuring the UV-visible spectrum of the solution. UV-visible spectrum was monitored on Cary Series UV-Visible spectrophotometer Agilent Technology, operated within the wavelength range of 200 to 800 nm.

2.5 FT-IR Spectroscopy Measurement

The present study was carried out on *Mangifera indica* leaves extract and on the cobalt nanoparticles. FT-IR measurement of the samples was performed using FTIR-Cary 630 Fourier Transform Infrared Spectrophotometer, Agilent Technology, in a transmittance method at a resolution of 8 cm^{-1} in potassium bromide (KBr) pellets in the wave number range of 4000-650 cm^{-1}.

2.6 Scanning Electron Microscopy (SEM) Analysis

Morphology of the nanoparticles was studied using SEM analysis using electron magnification of 80 - 150,000x (MODEL-PHENOM ProX Scanning Element Microscope manufactured by Phenom World Eindhoven, Netherlands).

2.7 X-ray Diffraction (XRD) Analysis

XRD (PAN analytical, Netherlands) patterns were obtained with a diffractometer (Empyrean Model, Netherlands) operated at a voltage of 45 KV and a current of 40 mA using Cu-K(alpha) radiation in a -2 configuration with a wavelength (λ) of 0.1541. The sample was made smoother and was imparted on a slide which was then charged into the machine after adjusting the machine parameters and was operated via a monitor [10].

2.8 Colorimetric Detection of Mn (II) Ions Using Cobalt Nanoparticles (CoNPs)

According to Sithara et al. [11], to confirm the practical application capability of CoNPs probe prepared from *Mangifera indica* leaf extract, the concentration of Mn^{2+} in simulated wastewater sample was determined. Different concentrations of the Mn^{2+} ranging from 5 – 25 mM was used in a prepared colloidal CoNPs. 2 mL of the prepared colloidal of CoNPs was added to 2 mL of the different concentrations of the Mn^{2+} and was kept for 15 mins before determining different absorbance of the different concentrations with respect to different wavelength using a colourimeter.

3. RESULTS AND DISCUSSION

3.1 UV-visible Spectroscopy

The reduction of cobalt ions present in the aqueous solution of cobalt chloride during the reaction with *Mangifera indica* leaf extract occurred at 314 nm as shown in Fig. 1. The maximum absorption obtained at 314 nm is an indication of the surface plasmon absorption of cobalt nanoparticles confirming their formation.

3.2 Fourier Transform Infrared Spectroscopy

The FTIR analysis was carried out on *Mangifera indica* leaf extract before and after synthesis of the cobalt nanoparticles. FTIR measurements were used to identify the possible functional groups responsible for the reduction of cobalt ions to cobalt nanoparticles. Table 1 and Fig. 2 show the functional groups present in the leaf extract before synthesis while Table 2 and Fig. 3 show the functional groups present in the leaf extracts after synthesis of the cobalt nanoparticles. The main difference in the FTIR result of the *Mangifera indica* leaf extract before and after the synthesis of the cobalt nanoparticles is indicated by the absence of the carbonyl functional group with peak at 1733.2 cm^{-1} on Table 2 and Fig. 3.This can be attributed to the fact that the carbonyl functional group is oxidized to the carboxylic function (COO^-). The absence of the O-M-O bond vibration which appears in the range 1000-450 cm^{-1} indicated that there was no bonding between the cobalt and the acid. This can be explained by the fact that the cobalt (ii) ions were reduced to cobalt nanoparticles while the carbonyl in the extract was oxidized to the carboxylic ions which further dimerized.

The FTIR spectrum of cobalt nanoparticles as shown in Fig. 3 below indicated different peaks with different functional groups as shown in Table 2.

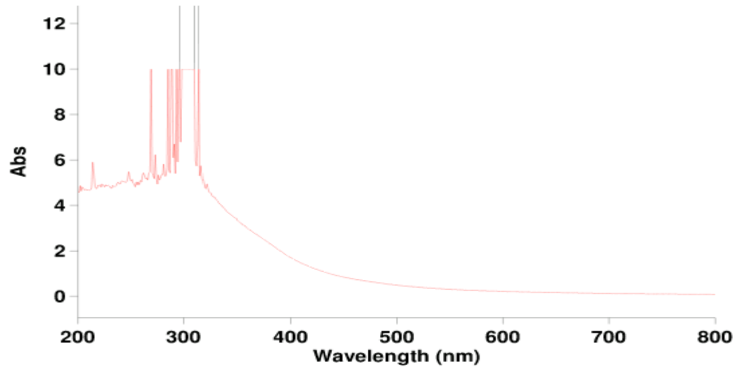

Fig. 1. UV-Visible spectrum of cobalt nanoparticles

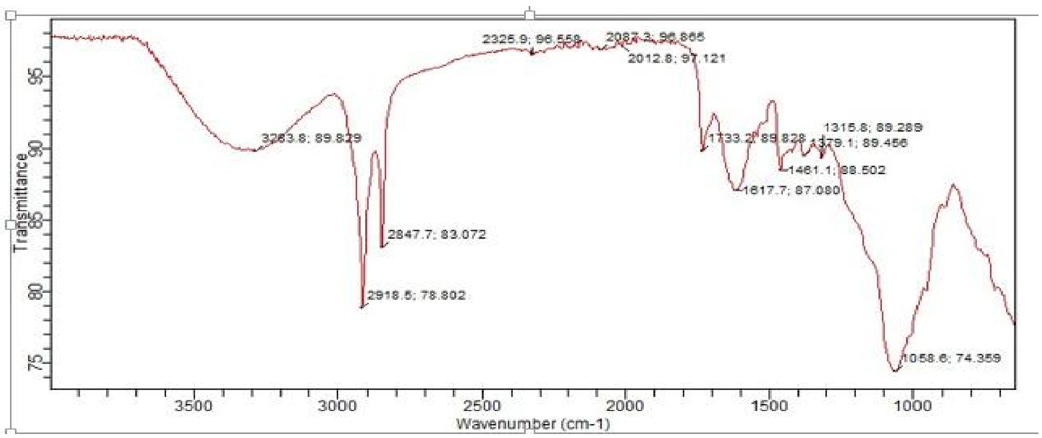

Fig. 2.The FTIR peaks of *Mangifera indica* leaf extract

Table 1. Functional groups of the leaf extract of *Mangifera indica*

Peaks (Wavelength in Cm^{-1})	Functional group
3283.8	O-H of alcohol
2918.5	C-H of alkane
1733.2	C=O of carbonyl functional group (aldehyde or Ketone)
1617.8	C=C of alkene
1058.6	C-O-C of ether
1461.1	C=O

Table 2. Functional groups of cobalt nanoparticles

Peaks (Wavelength in Cm^{-1})	Functional group
3276.3	O-H 0f alcohol
2922.2	C-H of alkane
1524.5	C=O of ketone OCO symmetric and asymmetric vibrations
1625.1	C=C of alkene
1218.8	
1032	C-O-C of ether

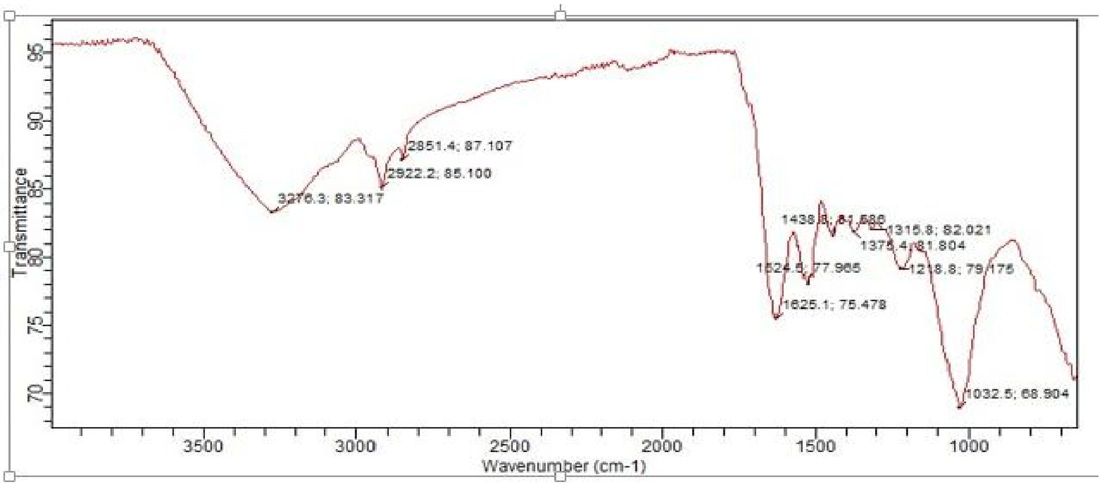

Fig. 3. FTIR of cobalt nanoparticles

Comparing the functional groups in both leaf extract and cobalt nanoparticles, it was observed that the peaks at 1733.2, 1461.1 and 1058.6 cm^{-1} were not featured in the FTIR of cobalt nanoparticles indicating that these functional groups were involved in the reduction of cobalt ion to cobalt nanoparticles.

3.3 Scanning Electron Microscopy Analysis (SEM)

The SEM images of cobalt nanoparticles are shown in Fig. 4 and Fig. 5. The morphology of the nanoparticles indicates irregular, cubic and pentagonal shapes of various sizes that are agglomerated. Further observations with higher magnifications reveal that these images possess smooth surfaces. At much higher magnification the images are seen as large particles which can be attributed to aggregation or clustering of smaller particles.

3.4 X-ray Diffraction Analysis (XRD)

Fig. 6 shows the XRD pattern of cobalt nanoparticles biosynthesized from the leaf extract of *Mangifera indica.* A number of Bragg reflections with the values of 6.21, 19.34, 23.02, 23.99, 34.89 and 43.68 within the angle range of 5.00 and 74.98 were observed. The XRD pattern

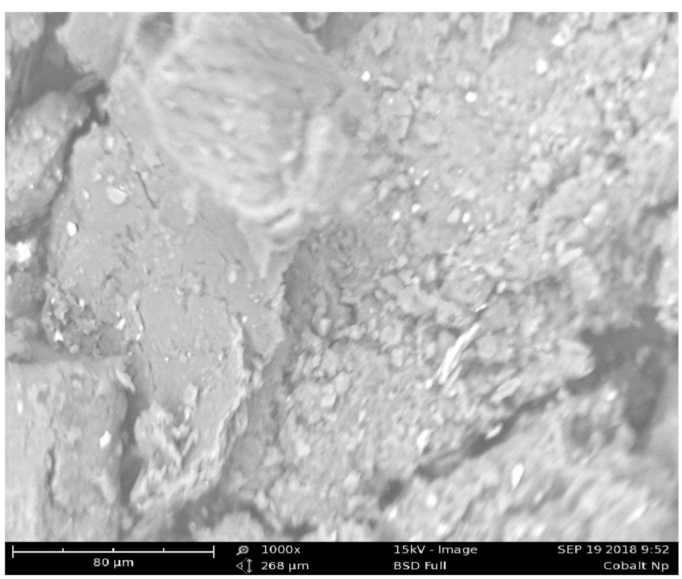

Fig. 4. SEM image of cobalt nanoparticles

indicates that the cobalt nanoparticles formed are crystalline in nature with a mixed phase structure (cubic, pentagonal and irregular) of cobalt nanoparticles. The average crystallite size of the cobalt nanoparticles was calculated from the width of the XRD peaks, assuming that they are free from non-uniform strains, using the Debye-Scherrer equation shown below in equation 1.

$$D = (K\lambda / \beta\cos\theta) \text{ ....Eq.1.}$$

Where D is the particle size (in nm), *K* is a constant equal to 0.9, λ is the wavelength of X-ray radiation (0.1541),β is the full-width at half maximum (FWHM) of the peak (in radians) and is the Bragg angle (in degrees). The average crystallite size was found to be in the range of 25-40 nm.

3.5 Colorimetric Analysis

Different concentrations of Mn (II) ions with the corresponding redshift of the UV-Visible spectra are depicted in Fig. 7. The colloidal cobalt nanoparticle was tested with various concentrations (5-25 µM) of Mn. (II) ions. It was observed that the absorption of the Mn (II) ions decreased at increased concentration of Mn (II) ions (Table 3) indicating that Mn (II) ion can be detected even at a very low concentration.

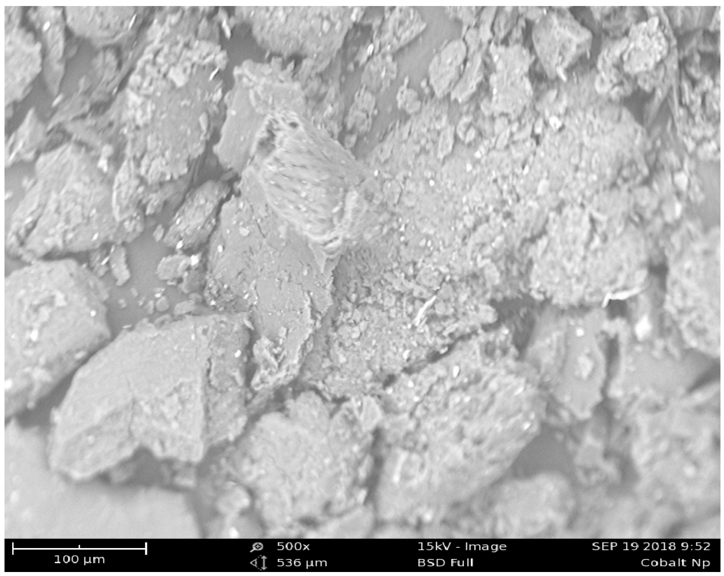

Fig. 5. Zoom SEM image of cobalt nanoparticles

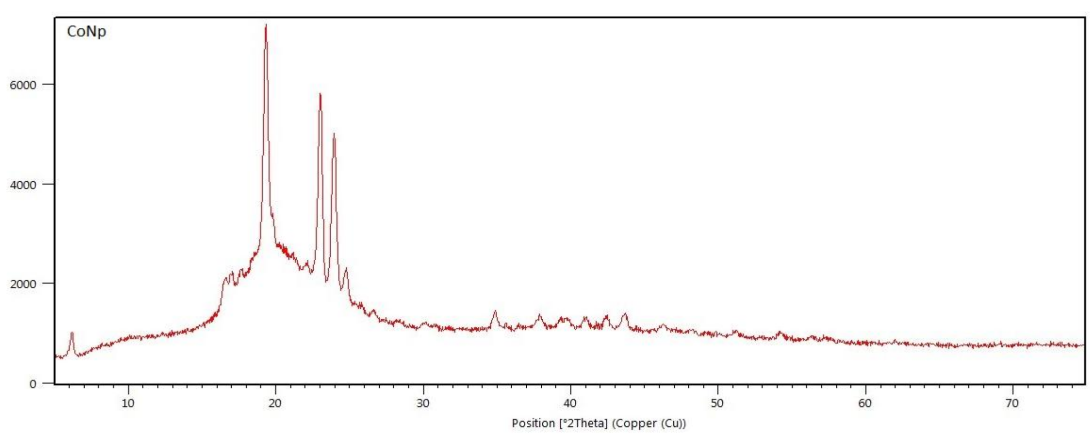

Fig. 6. X-ray diffraction pattern of cobalt nanoparticles synthesized from *Mangifera indica* leaves

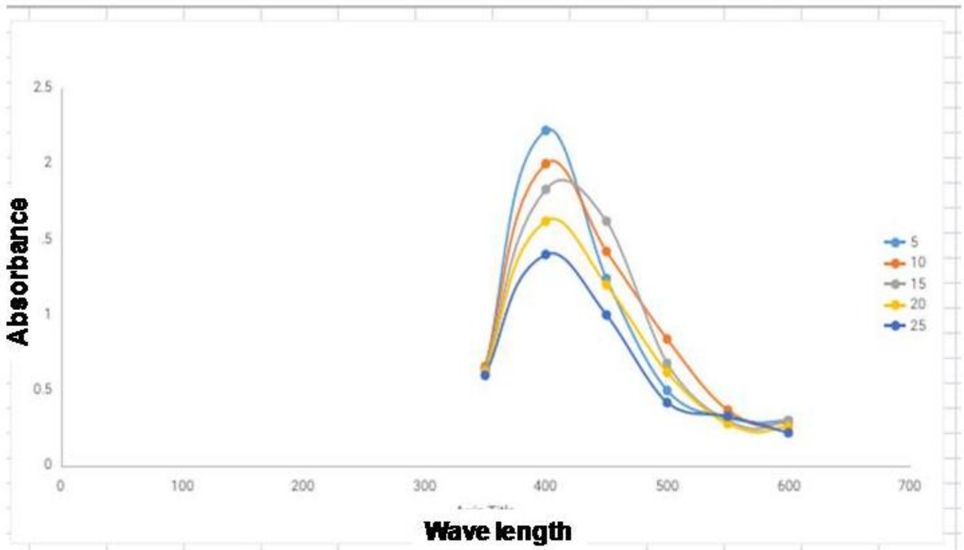

Fig. 7. UV-visible spectra of manganese (II) ions

Table 3. Absorption of Mn (II) ions with colloidal cobalt nanoparticle at different concentrations

Concentration (µM)	350 nm	400 nm	450 nm	500 nm	550 nm	600 nm
5	0.64	2..22	1.24	0.50	0.32	0.30
10	0.66	2.00	1.42	0.84	0.37	0.28
15	0.64	1.83	1.62	0.68	0.30	0.30
20	0.62	1.62	1.20	0.62	0.28	0.28
25	0.60	1.40	1.00	0.42	0.33	0.22

4. CONCLUSION

Characterization of the cobalt nanoparticles via UV-Visible, FTIR, SEM; XRD revealed maximum absorption at 314 nm which is a very good indication for surface plasmon absorption of cobalt nanoparticles. Different functional groups were observed in both the leave extract of *Mangifera indica* and cobalt nanoparticles synthesized with *Mangifera indica* and it was deduced that some of the functional groups were observed in a leaf extract did not appear in the cobalt nanoparticles indicating their usage in the formation of cobalt nanoparticles. The morphology of the cobalt nanoparticles indicated irregular, cubic and pentagonal shapes of various sizes with a smooth surface. The average crystallite size was found to be in the range of 25 - 40 nm indicating that the cobalt nanoparticle is within the nanoparticle. Application of cobalt nanoparticles in detecting Mn (II) ion in industrial wastewater was feasible because Mn (II) ion was detected even at a very low concentration.

5. RECOMMENDATIONS

Cobalt nanoparticle synthesized with *Mangifera indica* should be used in detecting other toxic heavy metals in industrial wastewater. Application of Green Chemistry in nanotechnology that is eco-friendly and cost-effective should be recommended for further use. Treatment of industrial wastewater with cobalt nanoparticle and other metal nanoparticles should be encouraged.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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Available:https://doi.org/10.1016/j.jare.2017.07.001

Peer-review history:
The peer review history for this paper can be accessed here:
http://www.sdiarticle3.com/review-history/48569