DETECTION OF MANGANESE (II) IONS PRESENT IN INDUSTRIAL WASTEWATER USING COBALT NANOPARTICLES SYNTHESIZED BIOLOGICALLY WITH *MANGIFERA INDICA* LEAF EXTRACT

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, crystalline in nature, with an average size of 25--40nm. The FT-IR analysis of the leaf extract reviewed some functional groups responsible for reduction of cobalt ions to cobalt nanoparticles while the SEM indicates that the synthesised cobalt nanoparticles possesses 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 indicating that Mn (II) ion can be detected even at a very low concentration. The minimum and maximum detection limit were found to be 5 and 25mM 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.

Key words: Mangifera indica, Mn^{2+}, cobalt nanoparticle, industrial wastewater, colorimetric detection.

1. INTRODUCTION

The unique properties of nanoparticles, especially in the size range 1-100nm, 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, many studies were conducted in controlling the size and shape of nanoparticles during the synthesis leading to the conclusion of the method of synthesis playing a major role. Though 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 need for alternative method of synthesizing nanoparticles which will not cause environmental hazards.

The green synthesized nanoparticles have gained prominence in recent years [2] which uses a variety of reducing agents including; cows milk, plant extract, microbes, and others [3]. 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 [4]. This prompted interest to synthesize cobalt nanoparticles using 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 have demonstrated antibiotics properties in vitro and are used in traditional medicine using the extracts of the bark, leaves, stems and unripe fruits [5]. Being cellulosic in nature can be used as an organic surface coating and stabiliser in this approach. In this work, cobalt nanoparticles was 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 colorimetric detection of Mn^{2+} from industrial wastewater was 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 Forestry Department of Michael Okpara University of Agriculture Umudike..

2.2 Preparation of aqueous plant extract:

The sliced leaves were washed thoroughlly with deionized water, air dried at room temperature for about two weeks and milled to a fine powder. About 25gramms of the powdered material was dispersed in a 250ml of deionized water in a 500 ml glass beaker and boiled at 80℃ 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, 100ml of the aqueous leaves extract was added to 900 ml of 1×10^{-3} M aqueous ($CoCl_2.6H_2O$) solution in a 1000ml bottle and was stirred for about 30mins. Within 48hrs 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℃ 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 1ml 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:

This 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 (MODEL -PHENOM ProX Scanning Element Microscope manufactured by PhenomWorld Eindhoven, the 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-Kα 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.

2.8 Colorimetric detection of Mn (II) ions using cobalt nanoparticles (CoNPs):

According to [6], 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 - 25mM) was used in a prepared colloidal CoNPs. 2ml of the of the prepared colloidal of CoNPs was added to 2ml of the different concentrations of the Mn^{2+} and was kept for 15mins before determining different absorbance of the different concentrations with respect to different wavelength using colorimeter.

3 RESULTS AND DISCUSSION

3.1 UV-visible spectroscopy:

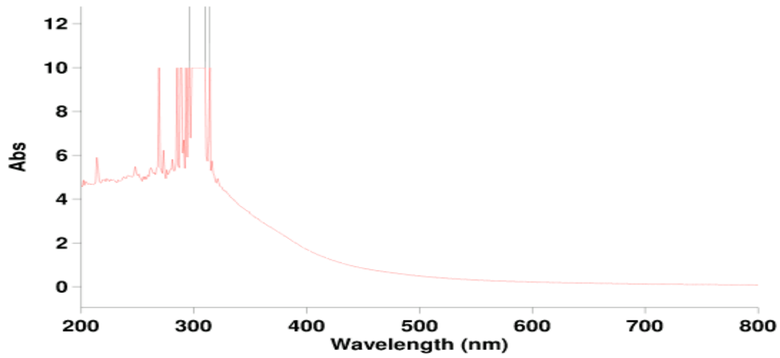


Fig. 1: UV-Visble spectrum of cobalt nanoparticles.

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 Figure 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 and on the synthesized cobalt nanoparticles. FTIR measurements were used to identify the possible functional groups (Table 1) responsible for the reduction of cobalt ions to cobalt nanoparticles. The result of FTIR analysis of the *Mangifera indica* leaf extract (Fig. 2) shows different bands at different peaks; .

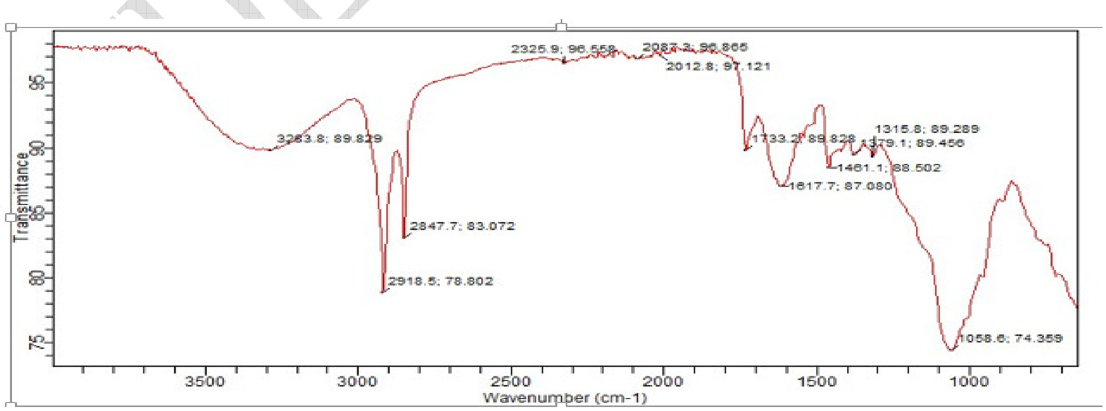


Fig. 2: The FTIR peaks of *Mangifera indica* leaf extract

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 aldehyde
1617.8	C=C of alkene
1058.6	C-O-C of ether
1461.1	C=O

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

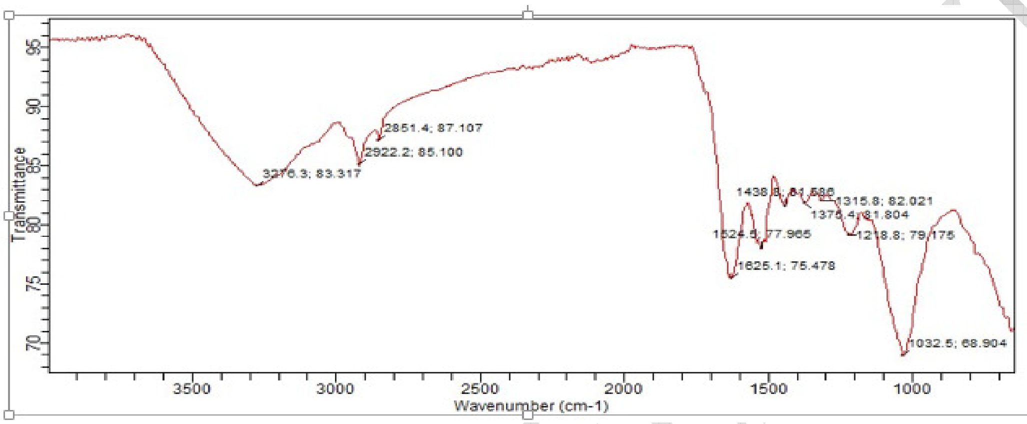


Fig. 3: FTIR of cobalt nanoparticles.

Table 2: Functional groups of cobalt nanoparticles

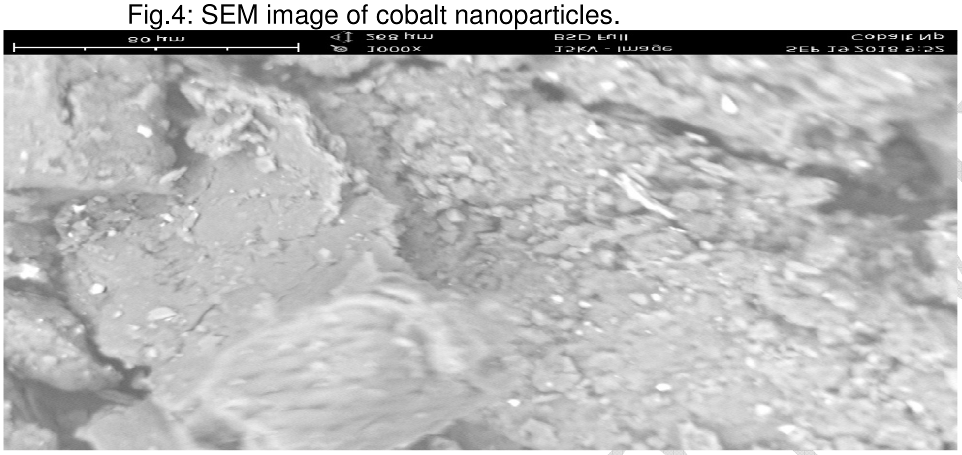
PEAKS (Wavelength in Cm^{-1})	FUNCTIONAL GROUP
3276.3	O-H 0f alcohol
2922.2	C-H of alkane
1524.5	C=O of ketone
1625.1	C=C of alkene
1218.8	
1032	C-O-C of ether

Comparing the functional groups in both leaf extract and cobalt nanoparticles, it was observed that the peaks at 1733.2, 1461.1 and 1058.6cm^{-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 analysi (SEM):

The SEM images of cobalt nanoparticles are shown in Figure 4 and Figure 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.

Fig.4: SEM image of cobalt nanoparticles.



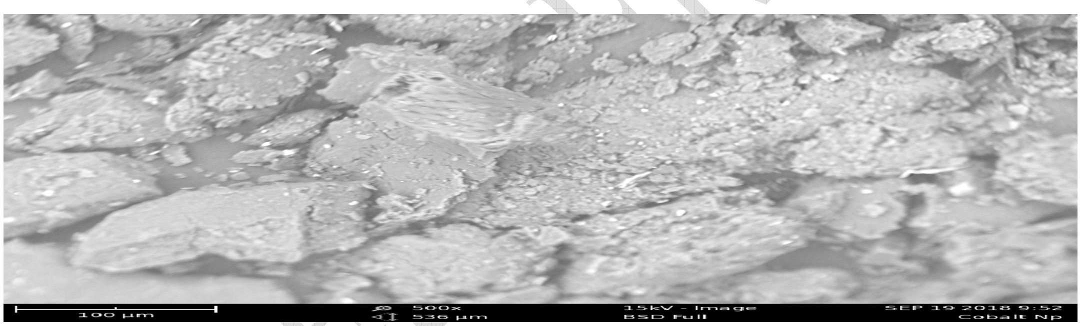


Fig. 5: Zoom SEM image of cobalt nanoparticles.

3.4 X-ray diffraction analysis (XRD):

Figure 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 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.

$$D = \frac{K\lambda}{\beta\cos\theta} \quad \text{...} \; 1$$

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 25-40nm.

Figure 6: X-ray diffraction pattern of cobalt nanoparticles synthesized from *Mangifera indica* l

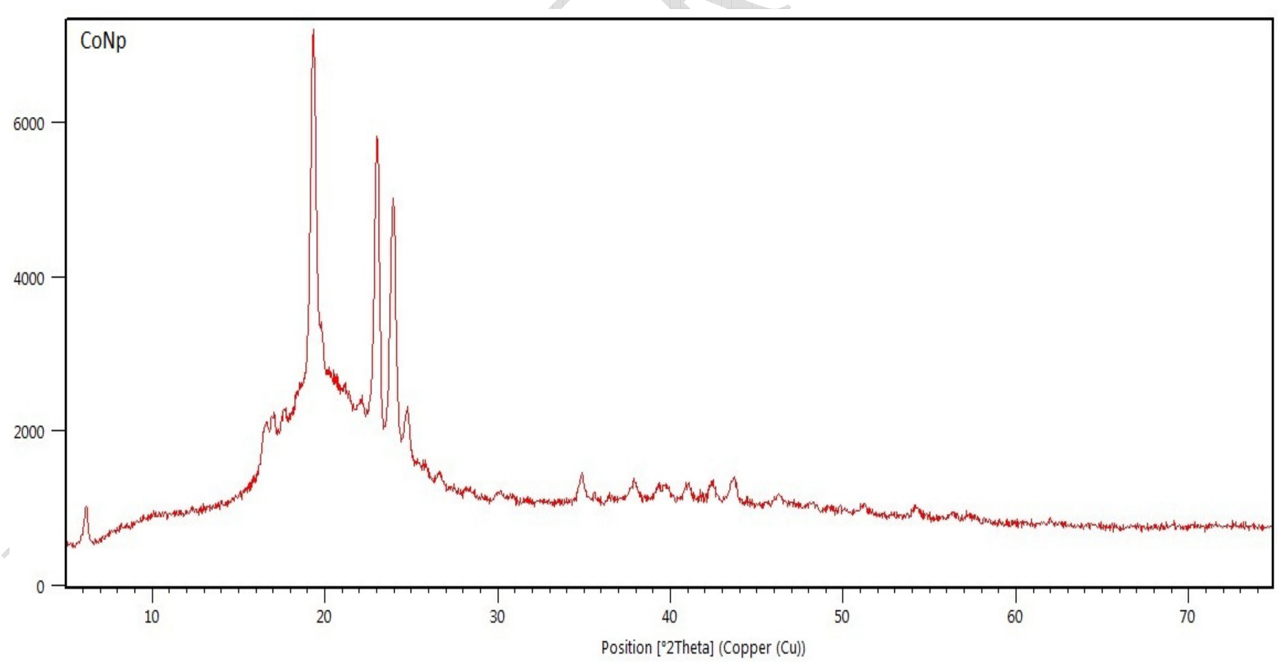
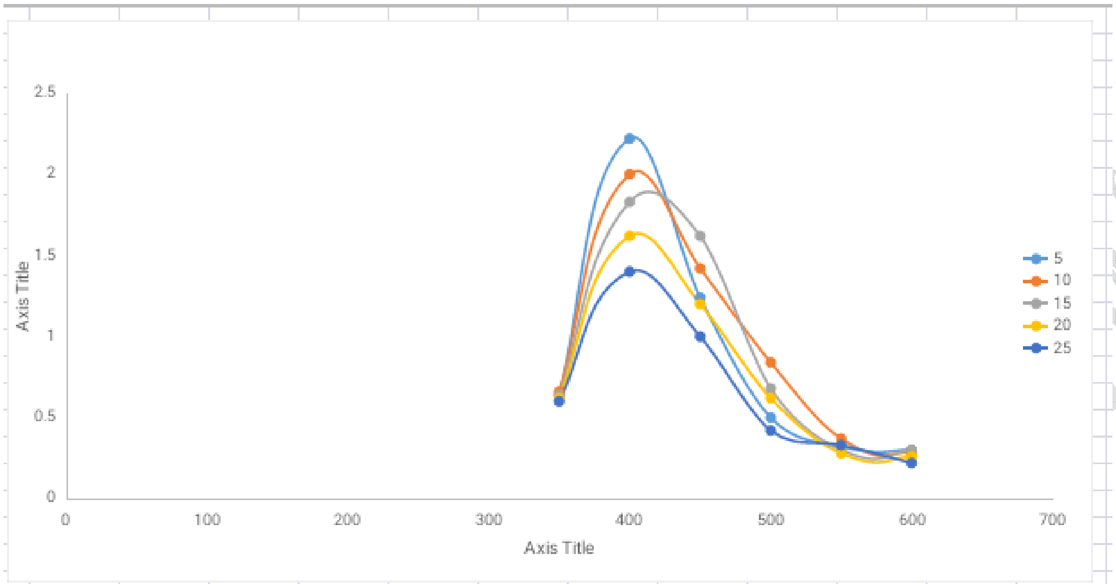


Figure 6: X-ray diffraction pattern of cobalt nanoparticles synthesized from *Mangifera indica* leaves.

3.5 Colorimetric analysis:

Different concentrations of Mn (II) ions with the corresponding red shift of the UV-Visible spectra is depicted in Fig. 7. The colloidal cobalt nanoparticle was tested with various concentrations (5-25µM) 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.



ABSORBANCE

WAVELENGHT

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)	350nm	400nm	450nm	500nm	550nm	600nm
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

Conclusion:

Characterization of the cobalt nanoparticles via UV-Visible, FTIR, SEM; XRD revealed maximum absorption at 314nm which is a very good indication for surface plasmom absorption of cobalt nanoparticles. Different functional groups where observed in both the leave extract of *Mangifera indca* and cobalt nanoparticles synthesized with *Mangifera indica* and it was deduced that some of the functional groups where observed in a leaf extract did not appeared 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 smooth surface. The average crystalline size was found to be in the range of 25- 40nm 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.

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 are 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.

REFERENCES

1.Nilesh SP; Raman PY. A Simple Biogenic Method for the Synthesis of Silver Nanoparticles using Syngonium podophyllum, an Ornamental Plant. MGM Journal of Medical Sciences 2016 3: 111 – 115. https://doi.org/ 10.5005/jp-journals-10036-1103

2.Ahmed S; Ahmad M; Swami BL.; Ikram S. A review on plants extract mediated synthesis of silver nanoparticles for antimicrobial applications: a green expertise. J. Adv. Res. 2016. 7: 17 28. https://doi.org/10.1016/j.jare.2015.02.0017

Selvakumar P; Viveka S; Prakash S; Jasminebeaula S; Uloganathan R. Antimicrobial activity of extracellularly synthesized silver nanoparticles from marine derived *Streptomyces rochei*. Int. J. Pharma. biological sci., 2012 3: 188 - 197. DOI://doi.org/10.22376/ijpbs

Khan I; Saeed K; Khan I. Nanoparticles: Properties, applications and toxicities. Arabian Journal of Chemistry. In press http://dx.doi.org/10.1016/j.arabjc.2017.05.011

Sha AL; Hassan RA; Alharbi AA; Alomavri T; Alamri H. Magnetic Hyperthermia using Cobalt Ferrite Nanoparticles: The Influence of Particle Size. Int. J. Adv. Tech., 2017 8, 196 . DOI: 10.4172/0976-4860.1000196

Sithara R; Selvakumar P; Arun C; Anandan S; Sivashanmugam P. Economical synthesis of silver nanoparticles using leaf extract of *Acalypha hispida* and its application in the detection of Mn(II) ion. Journal of Advanced Reearch 20178(6): 561 – 568. https://doi.org/10.1016/j.jare.2017.07.001