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Green Synthesis of Magnetite Iron Oxide Nanoparticles Using Stem Bark Extract of Prosopisafricana: Application for the Removal of Heavy Metals from Tannery Effluent

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ABSTRACT
Magnetite iron oxide nanoparticles (MIONPs) Fe_3O_4 were synthesized using aqueous stem back extract of Prosopis africana.The synthesis was done using iron (ii) chloride monohydrateand iron (iii) chloride (anhydrous)at 60^0C.The combination of color change and the result from the Uv-visible spectroscopic analysis confirmed the presence of MIONPs. The possible biomolecules responsible for the reduction of the metal salts were studied using Fourier Transform Infrared Spectroscopy (FT-IR). The crystalline nature of the MIONPs was studied using X-ray diffraction analysisand the surface morphology of the MIONPs was also studied using Transmission Electron Microscopy (TEM). The synthesized MIONPs were mixture of spherical and cubic shapes. The diameter range was between 0.88-2.25nm.The potential application of the MIONPs for the removal of heavy metals from tannery effluent was also explored.The removal efficiencies of heavy metals like Cr and Zn was 100%. The MIONPs showed excellent efficiency in the removal of toxic metals from the environment.

Keywords: Prosopis africana, green synthesis,magnetite iron oxide nanoparticles, Chromium removal, Zinc removal, Lead removal

I. INTRODUCTION

Nanotechnology is an active field of research and deals with matter at a nanoscale. Zero valent metallic nanoparticles like silver (Ag^0), Gold (Au^0), Platinum (Pt^0) and metallic oxide nanoparticles such as magnesium-oxide (MgO), titanium oxide (TiO_2), iron oxide (Fe_2O_3) nanoparticles and many more were reportedly synthesized. The term nanoparticle refers to a particle of size between 1nm-100nm. At the nanoscale, matter has entirely different properties compared to bulk materials. The small size gives them high surface area to volume ratio, which can be utilized in many areas like biomedicine [1], food industry [2], environmental bioremediation [3], energy storage [4] and aquaculture [5].

There are number of methods for the synthesis of nanoparticles which include physical, chemical and biological routes [6]. However, physical and chemical methods have limitations such as high cost, high energy consumption, low productivity and involve chemicals that are toxic to both humans and the eco-system [7]. On the other hand, biological route or green nanotechnology is preferred as an alternative for its simplicity, low cost, sustainability and more environmental friendly [8].

Iron oxide nanoparticles (IONs) have received global attention because of its magnetic property which is exciting. It was found that the surface area of the iron oxide particle has important effect on their magnetic properties [9]. IONs are widely used in reversing images in magnetic resonance technology [10], tissue restorations [11], detoxification of living fluid [12], delivering drugs within living systems [9], and the removal of toxic heavy metal ions from wastewater [13]. Iron oxide

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exists in different forms naturally, which are magnetite (α-Fe_3O_4), maghemite (γ-Fe_2O_3) and hematite (α-Fe_2O_3). Several physiochemical methods were used for the synthesis of IONs such as hydrothermal [14], sol-gel [15], thermal decomposition [16] and co-precipitation [17]. All these methods suffered same setbacks as aforementioned in both physical and chemical methods. Thus, a simpler, greener, cost effective and more environmental-friendly method is preferred.

Tannery industries (leather making industries from animal skin) discharge more toxic effluents than many industries and this exert negative influence on eco-system directly or indirectly [18].The tannery effluent is known for its high-colored, acidic and alkaline liquor [19]. Reports have shown that the tannery effluent discharged in Nigeria have higher concentration of heavy metals like Zn, Cr and Fe than the permissible limits [20].

Heavy metals are toxic metallic elements that have densities greater than 5.0g/cm^3 and example include Zn, Fe, Cu, Cr, Hg, Pb, Ni, Co, etc. [21]. These heavy metals cause various deadly diseases for example cancer of the blood (As), damage to the brain, nervous system, red blood cells (Pb) and Cr poses high risk of dermatitis to human [22].

Prosopis africana, african mesquites or iron tree is the only Prosopis species native to tropical Africa. P. africana is a flowering plant from the family of Leguminosae-mimosoideae and genus Prosopis. Different names of the plant in various languages in Nigeria include Kiriya (Hausa), Ayan (Yoruba), Ibwa (Igbo), Okpehe (Idoma) and Kpaaye (Tiv). P. africana has an average height of 4-20m with an open crown and slightly rounded buttresses. The bark is dark, scaly and red-brown with white streaks. It occurs from Senegal to Ethiopia in the zone between the Sahel savanna forests. Due to its extreme exploitation, it has disappeared from many parts of the Southern Sahel and the adjacent Sudan savanna [23]. Specifically, P. africana can be found in northern Nigeria e.g Kano, Kaduna, Katsina, Jigawa, Niger, Zamfara, Sokoto, Plateau, Borno, Gombe, Bauchi etc. where the seeds when fermented serve as food condiment due to its high contents of proteins and fatty acids (Agboola, 2004).

II. MATERIALS AND METHODS

2.1Chemicals and Sample Collection

The precursors, iron (ii) chloride monohydrate, iron (iii) chloride and sodium hydroxide wereof analytical grade and purchased from Sigma Aldrich. All solutions were made using doubled distilled water. The sample, stem bark of Prosopis africana was collected from Dogon Kawo village, Doguwa Local Government, Kano State Nigeria. Identification and authentication of the sample were done at the Herbarium Unit of Plant Science Department, Bayero University Kano, Nigeria. A certificate with a voucher numberBUKHAN0193 was given.

2.2 Preparation of Prosopis africana Stem Bark Extract (PASE)

The sample was washed using distilled water to remove dust impurities, shed-dried and pulverized. The powdered sample was stored in a sample bottle in the Chemistry Laboratory of Science Laboratory Technology Department, Federal Polytechnic Offa for later use.

2.3Prosopis africana Stem Bark Extract Preparation (PASEP)

Twelve gram (12g) of the powdered sample was measured, transferred to a big beaker and 120cm^3 of doubled distilled water was added and heated until boiled. It was then filtered using Whatman no. 1 filter paper. The filtrate was light brown in color.

2.4 Preparation of Precursor Solution [($FeCl_2.H_2O$) and $FeCl_3$]

About 3.2g iron (ii) chloride monohydrate and 8.1g ofiron (iii) chlorideswere transferred to 250ml volumetric flask containing about 100ml of doubled distilled water. The mixture was stirred and heat was applied slowly. For precipitation, about 3.2g of NaOH was dissolved in 50mL volumetric flask.

2.5 Synthesis of Iron Oxide Nanoparticles

To 50cm^3 of the precursor solution, 15 mL of the prepared stem bark extract of Prosopis africana was added in stepwise.Upon mixing the two solutions, the color changed immediately to brown and became darker progressively. 50mL solution of NaOHwas used to precipitate the synthesized nanoparticles. The mixture was stirred at 60^{0}C using magnetic stirrer at 450rpm for about 40 minutes. Isolation of the nanoparticles obtained was achieved by centrifugation at 7000rpmfor about 10 minutes. This wasfollowed by multiple washings using doubled distilled water and then oven dried at 60^{0}C for 72 hours.

2.6 Collection of Tannery Effluent Sample

The sample of the tannery effluent was collected from freshly discharged effluent from a

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tannery industry in Chalawa Industrial Estate, Kano State Nigeriausing a plastic container. The plastic container was previously washed with detergent, soaked in 10% $HNO_3$and rinsed with double distilled water. Suitable volume of the collected sample was acidified with concentrated HNO_3toavoid precipitation and maintain the metal ions in their respective oxidation states. The pH of the sample was brought down to 2.0 due the acidification.

2.7 Digestion of the Effluent Sample

To about 100mL of the sample, 2mL of concentrated H_2SO_4 and 1mL of concentrated HCl were added followed by heating to about 80^0C for digestion in fume cupboard. The heating was stopped when the volume of sample aliquot reached 20mL. The set-up was allowed to cool down. The content wastransferred to 50mL volumetric flask and topped to the mark using doubled-distilled water. This was followed by filtration (EPA, 1987).

2.8 Application for the Removal of Heavy Metals

For the application, two separate volumes of the iron oxide nanoparticles (5mL and 10mL) labeled as **S1** and **S2** were measured in two different 50mL volumetric flasks and topped to the marked using double distilled water. 50mLof the previously prepared nanoparticles solutions (**S1** and **S2**) were mixedwith 150 ml of the tannery effluent sample in two different flasks to give to total volumes of 200mL per flask. The resultant solutions were homogenized using magnetic stirrer at 300rpm for 20 minutes.

For the quantification of the heavy metals (**Cr, Zn and Pb**) after homogenization,5mL of each sample was added 10mL of HNO_3+3HCl for the digestion to a volume of 50mL. The digestion was stopped when the volumes of the aliquot reached 10mL, cooled and topped to the mark using doubled distilled water. The two solutions were carefully filtered. Both the initial and final concentrations of the heavy metals were determined using AAS technique.

2.9 Characterization of IONs

IMPLEN Uv-Visible spectrophotometer (C40, NPOS 4.2 build, version 14900, with serial number S40727) was used to monitor the growth formation of the nanoparticles. The spectrophotometer was calibrated in the range of 350-900nm. This analysis was done to determine the Surface Plasmon Resonance of the material under investigation. The possible biomolecules involved in the formation of the nanoparticles were studied using Fourier Transform Infrared (FT-IR) spectrophotometer (Agilent Cary 630 FTIR, USA). The crystalline nature of the nanoparticles was investigated using (Rigaku Miniflex with wavelength 1.54Å using (Cu-Kα1,2 radiation), 40kV and 15mA. The surface morphology of the nanoparticles was studied using Transmission Electron Microscopy (TEM)(TEM-ARM200F-G Verios 460L).

III. RESULTS AND DISCUSSION

3.1 Uv-visible spectroscopy Analysis

Figure 3.1 shows the absorptionbands of the iron oxide nanoparticle whichwas done in the range of 350-900nm. The immediate color change from light brown to dark brown indicates the formation of the nanoparticles due to the surface plasmon excitation vibrations [24]. This was confirmed by the presence of absorption bands at 368nm in the spectrum. The extract contained some metabolites that act as reducers and stabilizersto the metal salts.

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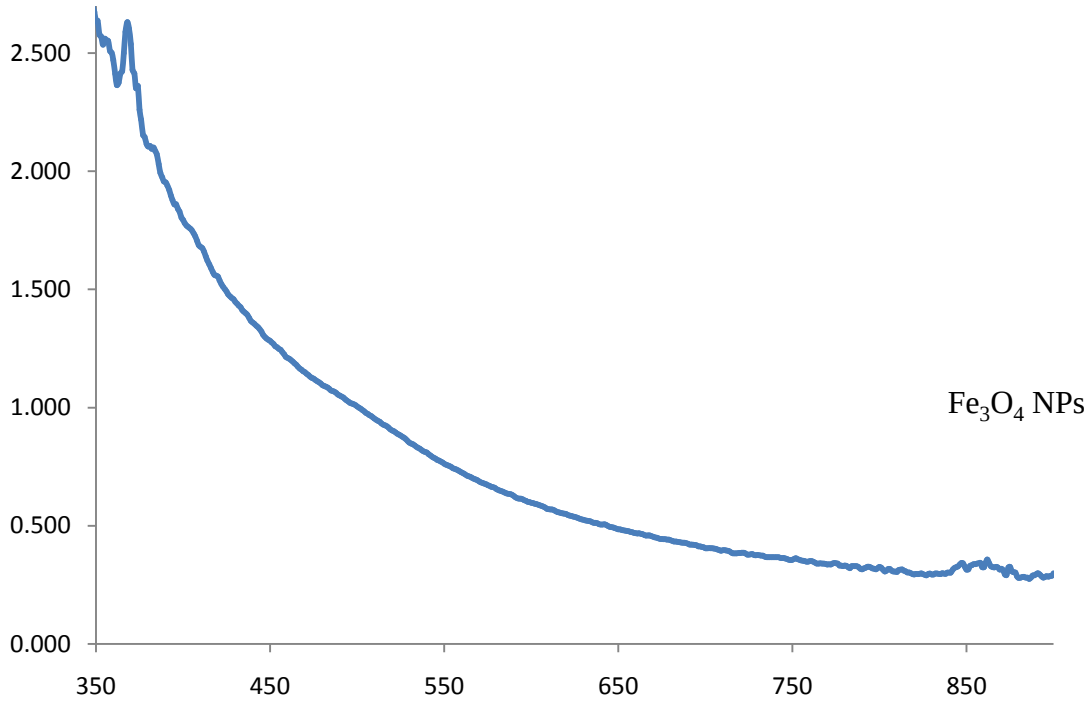

Figure 1: UV-Visible spectrum of synthesized MIONPsat 60^0C

3.2 Fourier Transform Infrared Spectroscopy (FT-IR)

Figure 3.2 shows the FT-IR spectrum of the biosynthesized nanoparticles. This analysis gives the probable biomolecules responsible for the reduction of the metal salts. The broad absorption at 3280.056cm^{-1} is attributed to the stretching of –OH group from phenolic or hydrogen bonded alcohols. The absorption at 1636.30cm^{-1}is assigned to a stretching of carbonyl compound C=O [25]. The absorptions at 633.64cm^{-1} and 536.73cm^{-1}approximately corresponds to the Fe-O bondstretches as reported byBuarki et al. [26].Polyphenols and phenyl groups play a major role in reducing iron ions to iron oxide nanoparticles [27].

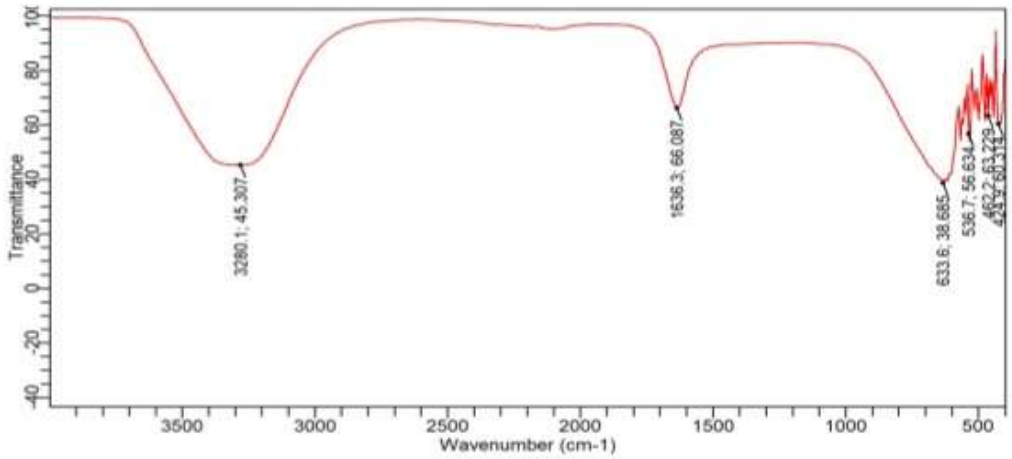

Figure 3.2 FT-IR spectrum of the biosynthesized MIONPs

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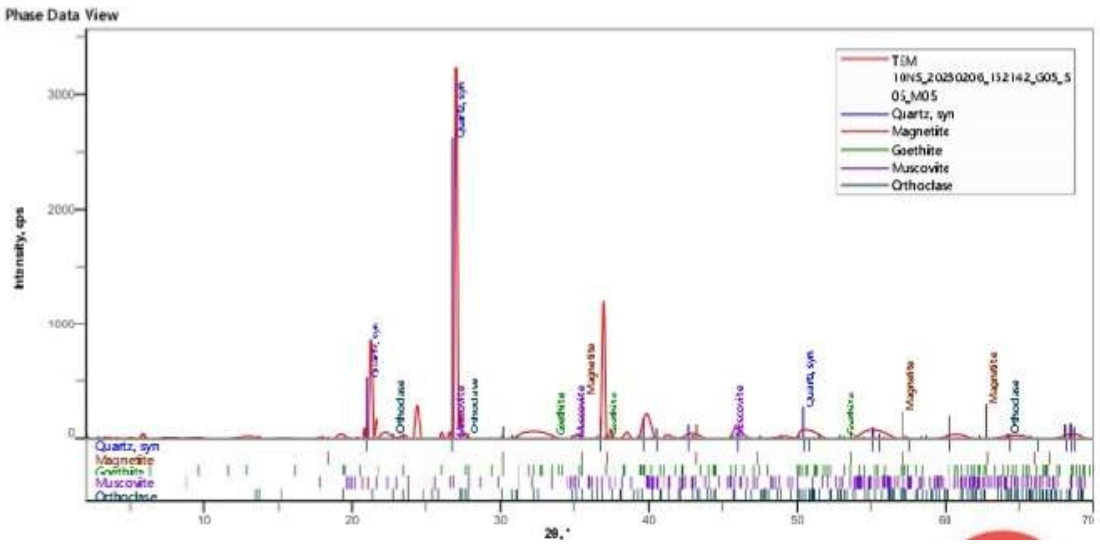
3.3 X-ray diffraction analysis

Figure 3.3 (a) and (b) show the XRD spectra of the synthesized nanoparticles using Prosopis africana aqueous stem bark extract.The presence of prominent peaks at 2Θ = 35.0^0, 54.2^0 and 63.1^0corresponds to the crystalline planes **(311), (422), and (440)**, respectively, which are assigned to the magnetite magnetic phases (Fe_3O_4) as reported byKarin et al. [28]. The DB card file number for the magnetite magnetic phases is **00-001-1111**. Other strong peaks include 21.18^0, 26.9^0, 36.9^0, 39.7^0, 50.4^0, and 55.2^0 corresponding to the crystalline phases of quartz, goethite and muscovite respectively.

(a)



(b)

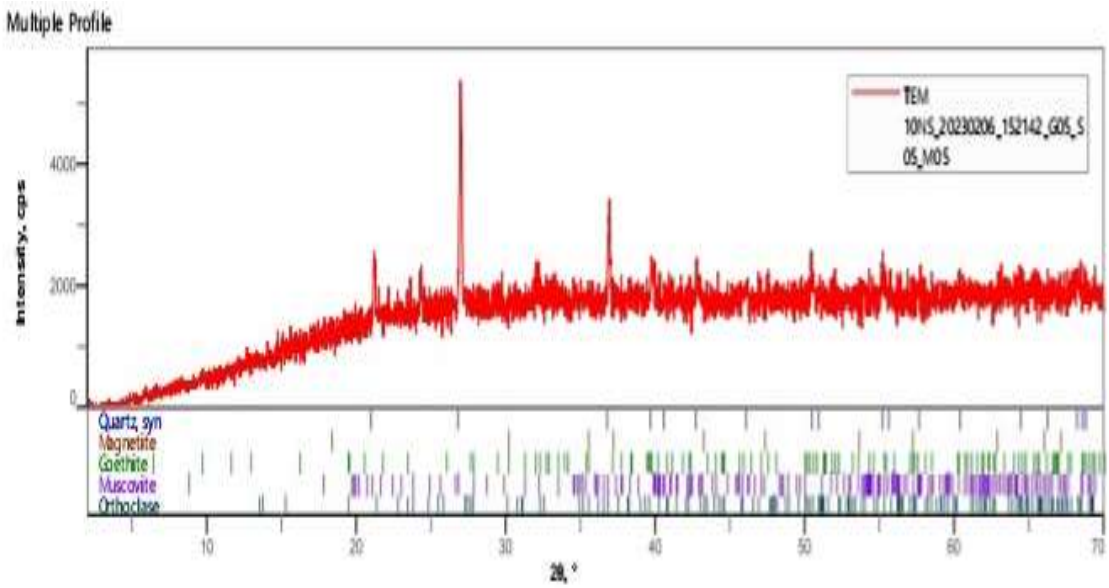


Figure 3.3 (a) and (b) x-ray diffraction spectra of the biosynthesized MIONPs

3.4 Transmission Electron Microscopy TEM

The surface morphology of the nanoparticles was studied using transmission electron microscopy. The image showed largely spherical and cubic shapes with sizes ranges between 0.88-2.5nm. The MIONPs were surrounded by green coating. The spherical shapes dominates.

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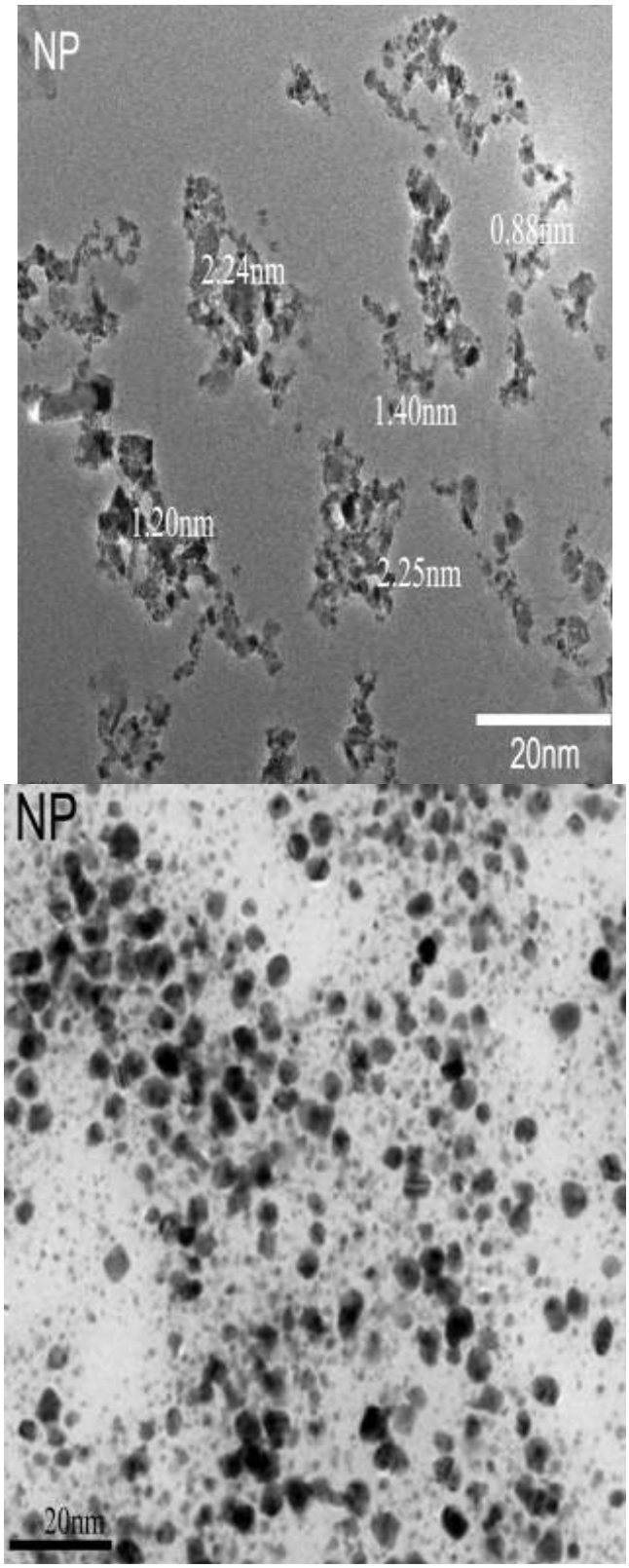

Figure 3.4 Transmission Electron Microscopy Image of the biosynthesized IONPs.

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3.5 Application for the Removal Heavy Metals Using AAS

Table 3.5 and **Table 3.6** show the initial and final concentrations of the heavy metals from the tannery effluent before and after application of the biosynthesized MIONPs. The concentrations give an idea of the quantity of each metal in the tannery effluent and the removal efficiency.

Table 3.5 SAMPLE S1(S1= 5ML OF MIONPs)

S/N	ii Element	Initial Concentration (ppm)	Final Concentration (ppm)	Removal Efficiency (100%)
1.	Chromium (Cr)	9.465	0.000	100
2.	Zinc (Zn)	0.694	0.000	100
3.	Lead (Pb)	0.45	0.312	31

Table 3.6 SAMPLE S2(S2= 10ML OF MIONPs)

S/N	ii Element	Initial Concentration (ppm)	Final Concentration (ppm)	Removal Efficiency (100%)
1.	Chromium (Cr)	9.465	0.000	100
2.	Zinc (Zn)	0.694	0.000	100
3.	Lead (Pb)	0.45	0.285	37

Thus, it is evident that the MIONPs were very efficient in the removal of Chromium (Cr) and (Zn) but less efficient for Lead (Pb). It was reported that the reducing agents have significant effect on the recovery of Pb ions [28].This is related to the formation of aggregates, due to theelectrostatic interactions of the biosorbent that decrease the availability of surface area to allow biosoation[30]. This proves the stability and increase of Pb concentrations that were found in this investigation, since only the same concentration of biomaterial was used and there were no differences.

The contact time is also a factor as only 20 minutes was used for the Pb removal. According to previous research, the ability to remove Lead depends on the increase of contact time from 30-60 minutes [31]. This explained why only 25% and 35% of Pb was removed.

IV. CONCLUSIONS

Conclusively, magnetite iron oxide nanoparticles were successfully synthesized using the aqueous stem bark extract of Prosopis africana. MIONPs were characterized using Uv-visible spectroscopy, Fourier Transform Infrared Spectroscopy (FT-IR), X-ray diffraction (XRD), and Transmission Electron Microscopy (TEM). The application for the removal of heavy metals from tannery effluent was also explored using AAS. The MIONPs were very efficient for the removal of Cr and Zn, but less efficient for Pb. The MIONPs is highly considered a potential in environmental pollution remediation of toxic heavy metals from tannery effluents.

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