Innovations

Application of Inorganic and Green Nanocomposite for the Cleaning of Toxic Metals Ions from Industrial Effluent Contaminated Water

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Abstract.

Current research findings in environmental sciences involved both integrative and collaborative technologies with a view of enhancing quality, cost reduction and creating ecological friendly approach upon application. The aim of the study is the application of inorganic and green nanocomposite for the cleaning of toxic metal ions from industrial effluent contaminated water using a synthesized silver nanoparticle from Scleorocaryabirrea stem bark extract. In this study, silver nanoparticles (AgNPs) were synthesized and characterized with UV-Vis absorption spectrophotometer, scanning electron microscope (SEM), an electron diffraction spectrophotometer (EDS) and X-ray diffraction (XRD)and transmission electron microscope (TEM). The surface shape, the composition,the crystallinity and biogenic structure ofthe AgNPs were revealed by SEM, EDS, XRD and TEM respectively. Columns were packed with synthesized AgNPs, gravel and the simulated industrial waste water containing four different heavy metals (Pb, Co, Cr and Ni) and were made to pass through the burrettes. The concentrations of metals before column analysis were analyzed with atomic absorption spectroscopy (AAS). The concentrations (mg/L) before and after the metallic absorptionPb (10.0, 15.0, 25.0), Co (1.0, 2.0,3.00), Cr (2.0; 4.0, 6.0), Ni (0.50, 1.0, 1.50) and Pb (1.378, 1.541, 1. 786) Co (0.741, 0.872, 0.919), Cr (0.017, 0.027, 0.046) and Ni (0.362, 0.130, 0.090)were estimated accordingly. The percentage heavy metals removal ranges from

25.9 to 99. 3 % for Co (1.0 mg/L) and Cr (4.0 mg/L), respectively. The findings showed an enhanced and effective adsorbent ability at a higher concentration of heavy metals in the contaminated water source and were however, less effective in the adsorbent capacity at a low concentrations of the metals. This suggests the efficacy of a modified natural product in the curtailment of environmental pollution. Hence, S. birreastem bark synthesized NPs is recommended for cleansing a highly contaminated heavy metals containing water for healthy water usage.

Keywords: *Green synthesis, nanoparticles, wastewater, atomic absorption spectroscopy and toxic metals.*

Introduction

Water pollution is a global issue that requires a considerable attention. The increase in the anthropogenic activities result to discharge of organic and inorganic pollutants into the water bodiesthat causeadverse effects on human and aquatic biota (Yahaya*et al*., 2012; Yahaya*et al*., 2020; Egbosiuba*et al*., 2021). In recent times, contamination of water due to the presence of toxic heavy metals such as mercury, lead, arsenic, cadmium, chromium and copper are of great concern. Owing to their bioaccumulation in human, several health issues and irritating symptoms such as impairements of cognitive ability, cancer, nausea, low rate of metabolism(Li *et al*., 2002; Wang *et al*., 2007; Wang *et al.,* 2020; Fan *et al*., 2022), and other metabolic derangements can occur.

Several methods such as filtration, chemical precipitation, coagulation, reverse osmosis, membrane processes, microbial technology and among others have been applied for the removal of heavy metals. However, these techniques have been identified with shortcomings, such as ineffective removal of specific contaminants, production of harmful byproducts, expensive, slow in operation as well as difficulty in treatment approach(Mustapha *et al*., 2020; Muzaffar*et al*., 2018)and insensitivity nature of some instruments to heavy metal detection.

However,adsorption technology has been recently adopted due to the efficiency, cost effectiveness, limit toxicity, absence of sludge formation and availability ofdifferent types of adsorbents, either as in inorganic or green synthesized nanoparticles (NPs)derivativesat different levels of applications.

In principle, Nanomaterials (NMs) are various classes of small-scale particle with structural componentsthat are numerically less than 1000 nanometers (1 micrometer) in one dimensionscale (USSW EPA, 2010; Kumar et al., 2014). Nanoparticles (NPs) could also exist within 1 and 100 nm nano-size in at least in two dimensional system (EPA 2008; USSW EPA, 2010). NMs are classified based on their occurrences which could either be natural, incidental or engineered. Incidental NMs are by-products of other reactions (Kumar et al., 2010). The engineered class are

produced in the industries for either specified or various uses (USSW EPA, 2010; Peralta-Videa et al., 2011).
Currently, researchers have shifted towards nanomaterials (NMs)applications due to their minute size and big surface area that make them suitable for water treatment, biotechnology, drug delivery and among others(Muzaffar et al., 2018).
The green technique ofnanomaterials-based adsorbent such asAgNPs, TiO_2 NPs; Fe_2O_3 NPs,Fe_3O_4 NPs have been used by various researcher for the removal of toxic heavy metals from contaminated water, due to their high adsorption capacitydocumented in the literature (Verma*et al*., 2020; Arjaghi*et al.,*2020).Moreso, the ease of access to the sources (plant materials and basic chemicals commonly used in the routine laboratory practical delivery), a non toxic to human and the environment as it were projects nanoparticle a better candidate of choice for the heavy metal removal and other waste management technique on a large scale. This study has been optimized toward the application of inorganic and green nanocomposite for the removal of selected toxic metal ions (Pb, Cr, Co and Ni) from industrial effluent contaminated water using a synthesized silver nanoparticle from*Scleorocaryabirrea* stem bark extract, with detailed methodology and characterization techniques being discussed.

Collection of *S. birrea* stem

S. birrea stem bark was harvested from Jigawa State in Nigeria. Identification was done byMr Yusuf, a trained taxonomist at Federal University Dutse. The plant material was kept in the Biological Science Herbarium at the Federal University Dutse, while a voucher specimen number (Zafiya-002) was issued for reference.

Extraction of aqueous extract from the bark of *S. birrea*

Following the air drying of the stem bark of *S. birrea*at room temperature for 27 days, the dried sample was subjected to mechanically chopped and reduced into fine powdered via a Polymix, PX-MFC 90 D grinder. The cold maceration method was employed to remove the aqueous extract, this was done by soaking the pulverized powered (50 g) of the stem bark into 800 mL of water in a beaker (1000 mL) followed by agitation with an orbital shaker for 72 h. The resultant mixture was separated through filter paper (Whatman no. 1). The filtrates was then evaporated to dryness on a water bath at 40°C. The final concentrate was kept in a vial and preserved in the refrigerator at 4°C (Larayetan*et al*., 2020).

Synthesis and characterization of the synthesized silver nanoparticles (AgNPs)

A method as described by Larayetan*et al.*(2019), was employed for the synthesis of AgNPs from *S. birrea* extract. In this method,a freshly prepared aqueous solution of silver nitrate ($AgNO_3$, 1 mM) was prepared as a metallic solution. The solution containing *S. birrea* extract(200 mL) was mixed with 700 mL of silver nitrate solution and incubated on a hot plate under agitation using a magnetic stirrer for eight (8) hrs. The mixture was allowed to cool and centrifuged at 13, 000 rpm for 15 min, resulting in the formation of two layers. The upper layer, supernatant (a biosynthesized nanoparticle) was rinsed and dried at 40 °Cfor 48hrs of the study. The AgNPs was preserved at a room temperature for further investigation.

Characterization of synthesized AgNPs

The optical characteristics of the biosynthesized nanoparticle was investigated using UV-Vis absorption spectrophotometer (Perkin-Elmer Universival) that scanned the wavelength range of 200-600 nm. Employing a JOEL JSM-6490A. The produced AgNPs was analyzed using a scanning electron microscope (SEM) and an electron diffraction spectrophotometer (EDS) at several magnifications. The examination was conducted at a voltage of 15-20 kev on a two sided coated carbon stub. The surface shape and the composition of the AgNPs were revealed by SEM and EDS respectively (Arjaghi*et al*., 2021). The biogenic AgNPs were structurally analyzed via a transmission electron microscope (TEM) powered by JOEL 1210 operating at a working condition of 100 kv. After dissolving AgNPs in DMSO (Merck, Germany) and sonicating the solution for 20 minutes, a droplet of the suspension was applied to a copper surface covered with carbon grid and allowed to dry at room temperature before the examination was carried out. X-ray diffraction (XRD) through a Bruker D8 advanced X-ray diffractometer operating at 45 kv was used to check the crystallinity phase of the AgNPs at ambient temperature before analysis (Ajayi*et al*., 2021).

Preparation of Standards metal solution for calibration Curve

The analytical grade salts of the following heavy metals namely; Lead nitrate ($PbNO_3$), Cobalt chloride ($CoCl_2$), Chromium nitrate ($Cr(NO_3)_2$ and Nickel chloride ($NiCl_2$)were preparedinto stock solution (1000 mg/L) prior to serial dilution. They were used for the calibrations of atomic absorption spectroscopy (AAS), followed by determination of Pb, Co, Cr and Ni in the samples (El-Awady*et al*., 2021).

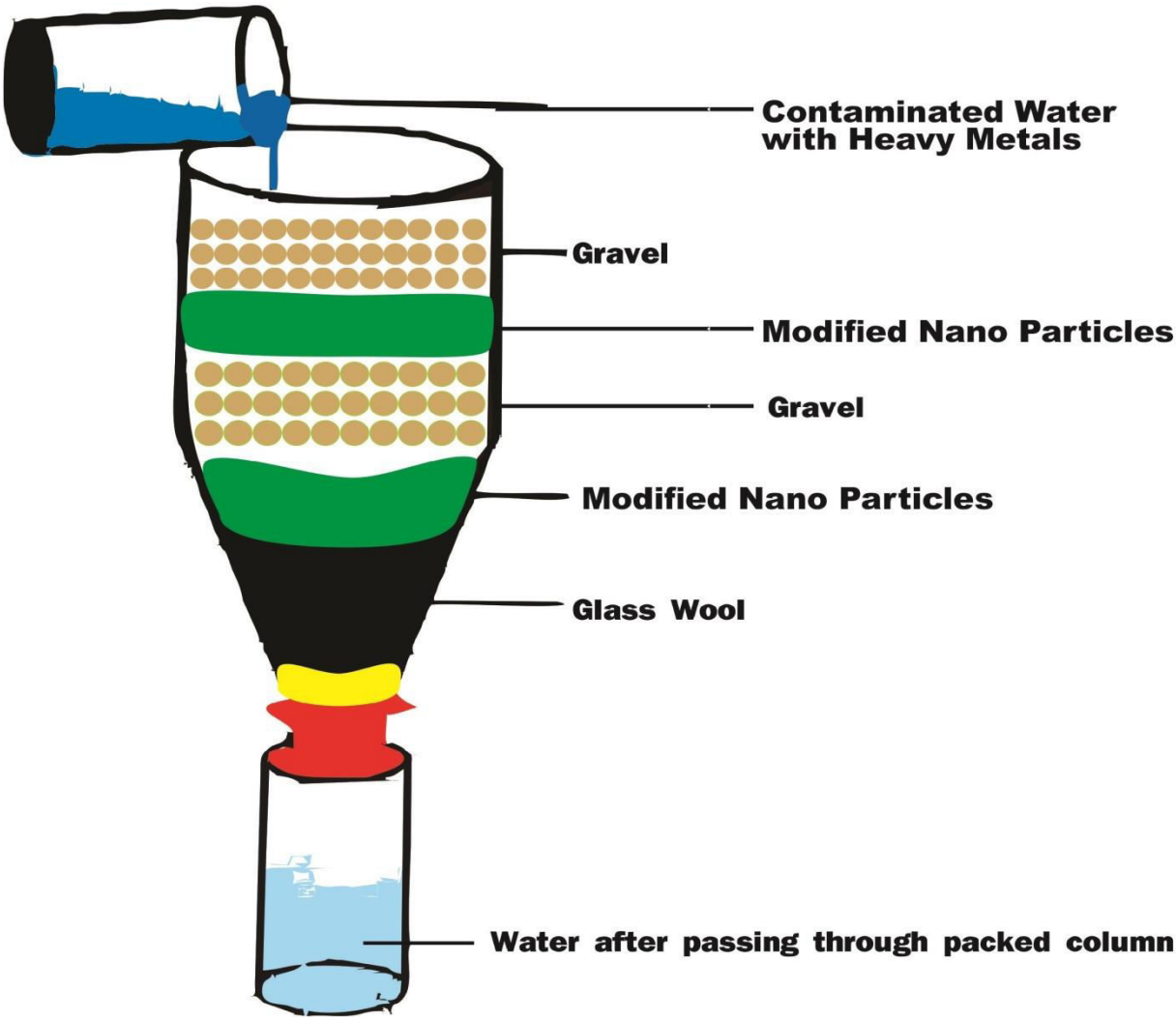

Figure 1. A packed column of different layers of modified NPs and gravel

An Easy multi-stage purification system

A burette was packed from the bottom (above the tap) to the top in the following order : A thick layer of glass wool, synthesized nanoparticle (NPs) , gravel (small size) , NPs and gravel and their thickness are 2.5cm and 4.0 cm respectively as show in figure 1. Three packed burrettes were used for each metal, for the treatment of stimulated industrial waste contaminated water. A total 12 of burrettes were used (That is three different concentrations of each metal). The concentrations of heavy metals in contaminated water samples were analyzed with AAS before and after passing through the packed column (El Awady et al., 2021; Egbosiuba et al., 2021).

The concentrations of Pb, Co, Cr and Ni were determined with SavantAA GBC atomic absorption spectroscopy (AAS) at wavelength of 217, 240.7, 357.9 and 232nm correspondingly. The adsorption isotherm (The rate of removal of metal ion) were determined with Langumir equation 1.

$$\mathrm{Re} = \frac{Ci - Ce}{Ci} \times 100 \qquad (1)$$

Where Re is the rate of removal of metal ion at equilibrium, Ci and Ce are the initial and equilibrium concentrations (mg/L) of metal solution respectively (Ahmed et al., 2013; Egbosiuba et al., 2021).

3. Results and Discussion

3.1. Spectrophotometric evaluation of $AgNO_3$ reduction

The most accurate and widely used method for identifying AgNPsproductionduring bthe initial phase of the plant biosynthesis is the UV-Vis absorption spectrophotometer. The addition of the aqueous stem bark of *S. birrea* extract to the colorless silver nitrate solution results in an alteration in color from light greyish to dark-greyish color and finally to a deep brownish coloration indicates that the $AgNO_3$ solution has been reduced to AgNPs (Ajayi et al., 2021). In addition, an absorbance peak of about 465 nm (Figure 1) may be seen in the UV-Vis absorption spectrum of the biosynthesized AgNPs. This UV absorption peak could be linked to the presence of some chromophores in the stem bark aqueous extract of *S. birrea* (Egbosiuba et al., 2021).

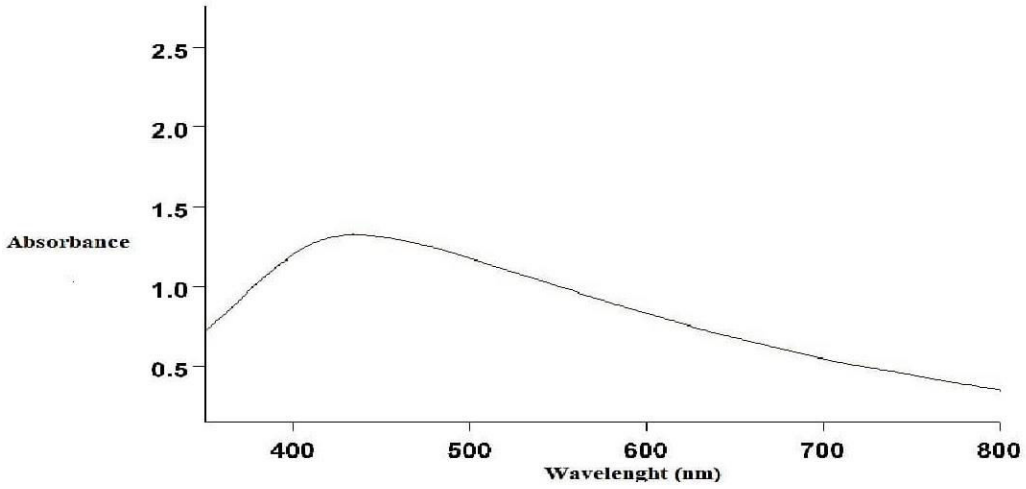

Figure 2: UV-Vis absorption spectrum of biosynthesized AgNPs

The biosynthesized AgNPs was subjected to SEM analysis so as to determine its form and composition (Figure 3). The SEM micrograph revealed the formation of spherically, triangular and irregularly shaped nanoparticles. The AgNPs biosynthesized were well diffused even though there were not many clusters of them , which may have been caused by the plant extract's uneven dispersion in the solution (Larayetan *et al*., 2019)

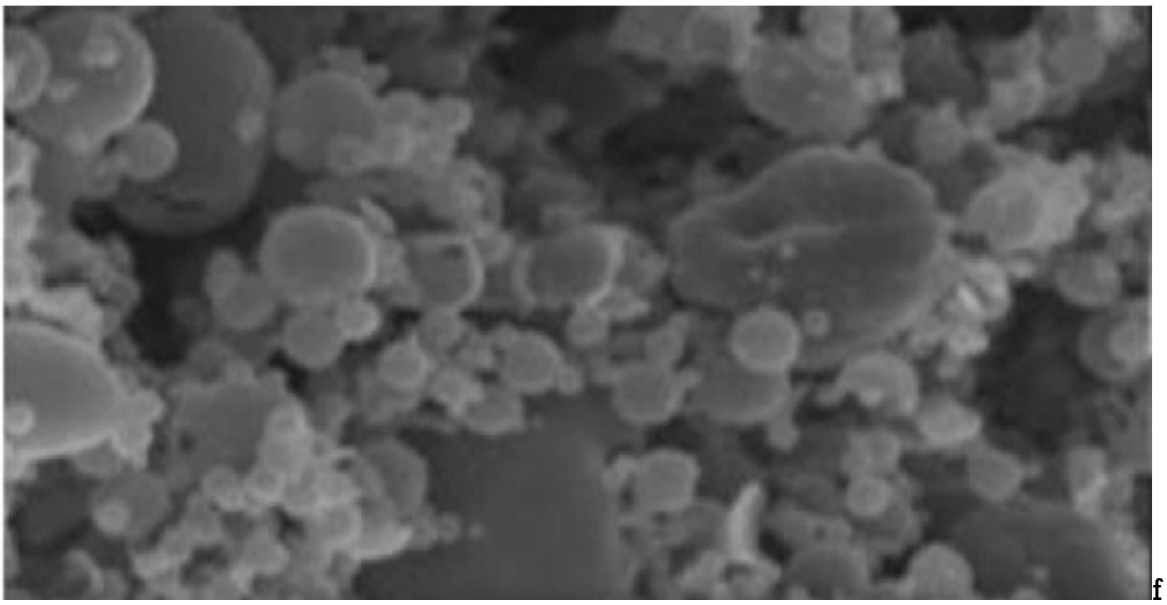

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Figure 3: SEM Image of AgNPs

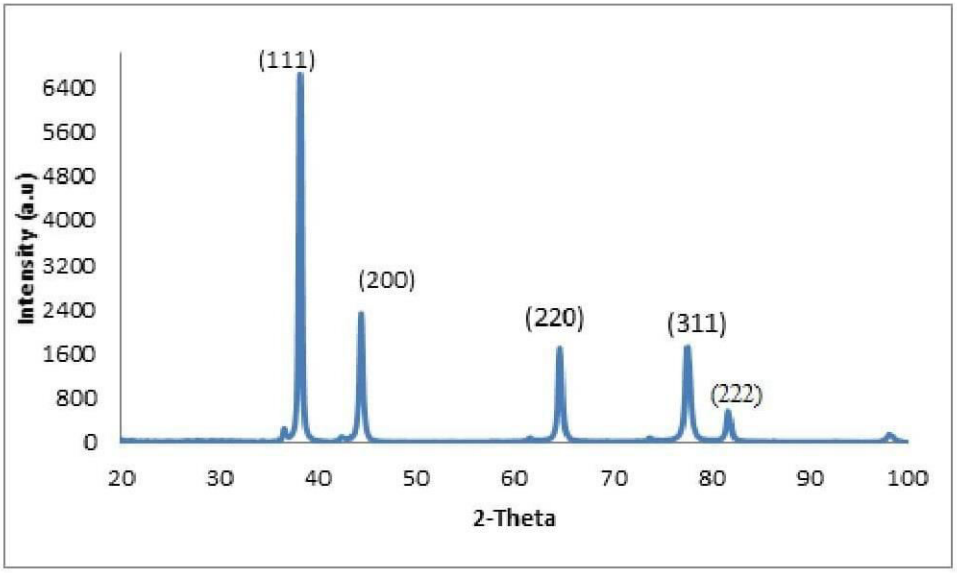


Figure 4: XRD Micrograph of AgNPs

As shown in Figure 4 XRD was employed to analyse the structural characteristics of the biogenic AgNPs. Figure 5 also shows the SAED pattern, which further established the crystal planes of the biosynthesized AgNPs obtained from stem bark extract of *S. birrea*, which corresponds to the characteristic XRD pattern with many diffraction peaks at 2θ= 38.47°, 44.62°, 64.97°, 77.87°,and 85.09°, corresponding to the crystal planes of AgNPs (220), (111), (200), (220) (311) and (222), respectively (Larayetan et al., 2020). The observed diffraction peaks are well matched with the face centered cubic structure of AgNPs. The peaks exhibited by the XRD in figure 4. were further established by the SAED pattern observed in figure 5.

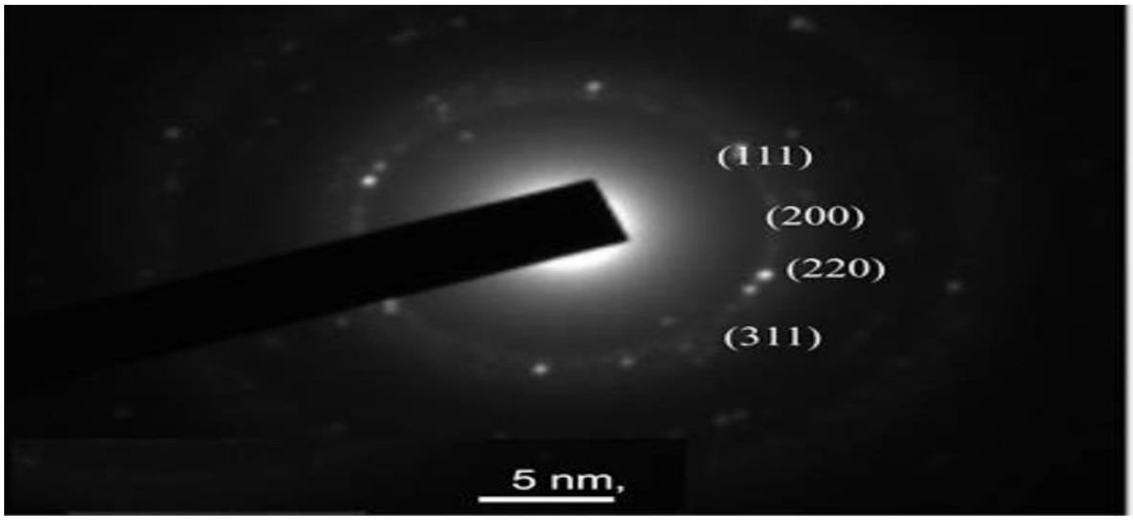


Figure 5: SAED Image of AgNps

EDS micrograph (Figure 6) showed the successful biosynthesis of AgNPs since silver metal has the highest peak in the EDS micrograph. Other peaks such as carbon, silicon, sodium, iron, sulphur, potassium and oxygen that appeared in the EDS image may be due to the secondary metabolites present in the stem bark extract of *S. birrea* used to bio-reduce the silver metal (Larayetan *et al*., 2019). Pure AgNPs were acquired after the bio reduction of silver nitrate salt ($AgNO_3$).

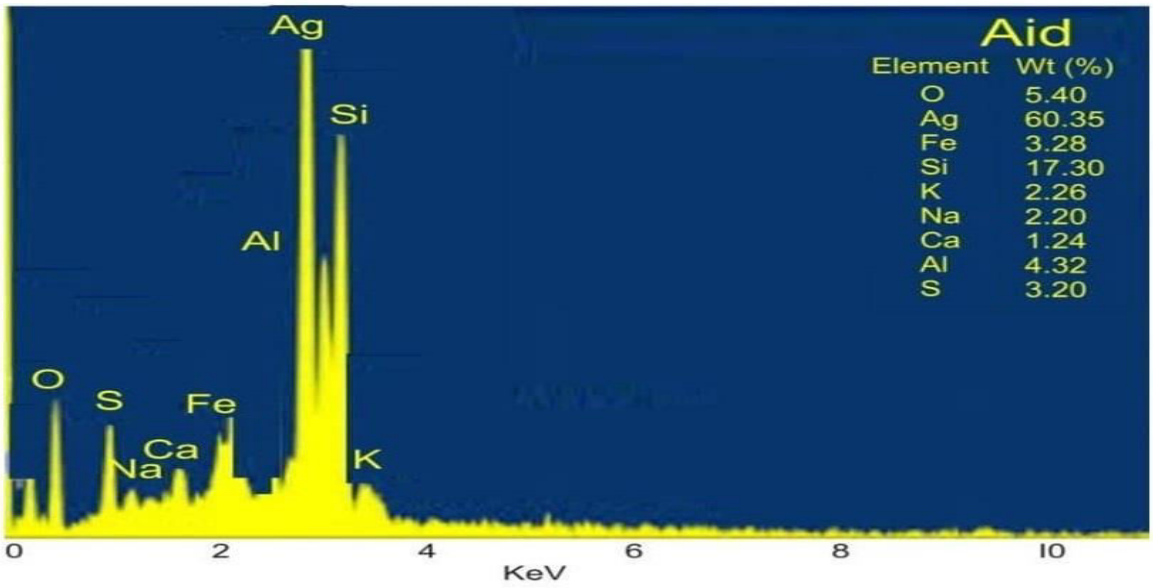


Figure 6: EDS Image of AgNPs

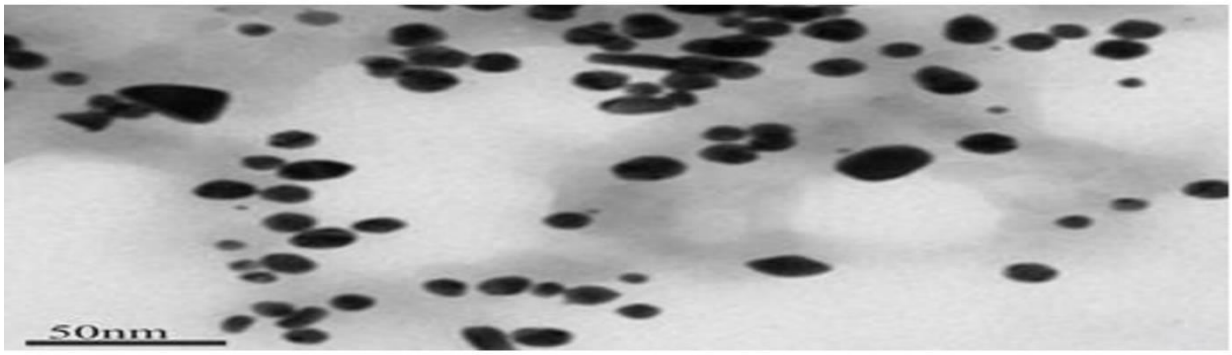


Figure 7: TEM Image of AgNPs of *Scleorocarya birrea*

TEM image of AgNPs was observed to establish the morphology and size of the synthesized material (Figure 7). It was discovered that a spherical shaped material was mainly formed. Other than these shapes, small amount of irregular Nano-shaped material was also formed. Size determination obtained from the average of the

measurement of the diameters of the individual particles by the instrument indicates that an average particle size of around 37 nm was obtained for this bio-synthesized material (Ajayi et al., 2021). The results of TEM, SEM, IR, UV spectrum and XRD are in conformity with previous work documented by Larayetan et al. (2019) and (2020); Ajayi et al. (2021) and Arjaghi et al. (2021).

Table 1. The concentrations of heavy metals in contaminated water before and after passing through the synthesized silver nanoparticles and percentage removal of the metals.

Heavy metals	**Conc. mg/L before Adsorption**	**Conc. mg/L After Adsorption**	**% of Removal (Re) of metal ion**
Pb	10.00	1.378	86.2
	15.00	1.541	89.7
	25.00	1. 786	92.9
Co	1.00	0.741	25.9
	2.00	0.872	56.4
	3.00	0.919	69.4
Cr	2.00	0.017	99.2
	4.00	0.027	99.3
	6.00	0.046	99.2
Ni	0.50	0.362	27.0
	1.00	0.130	87.0
	1.50	0.090	94.0

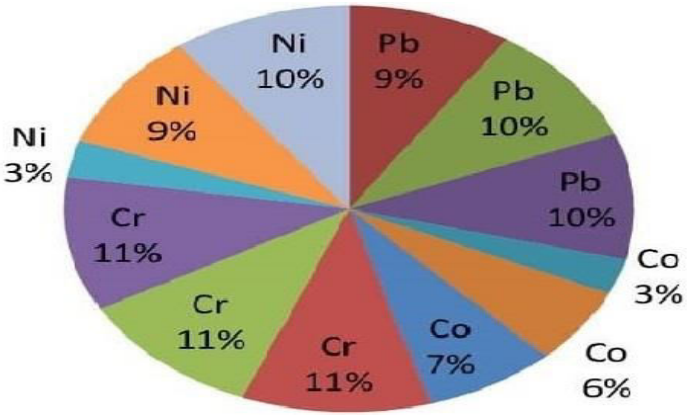
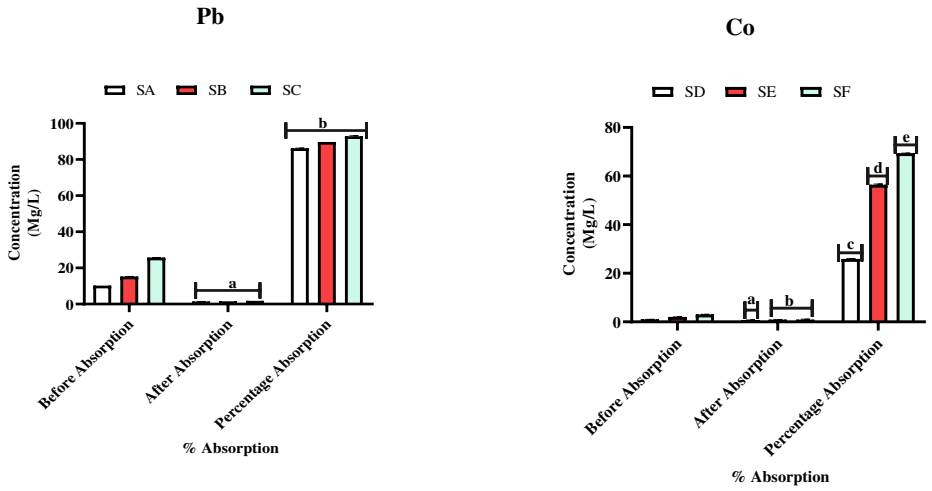


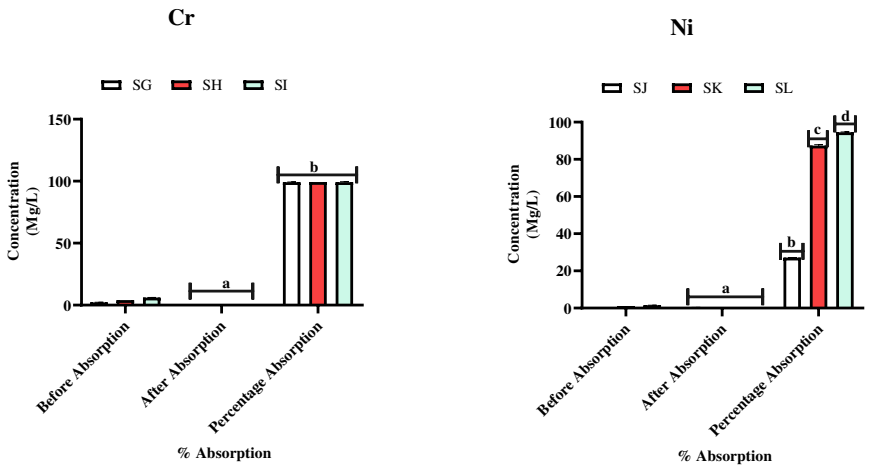
Figure 10: The order of removal of each metal at different concentrations

The percentage and order of removal of each metal at different concentrations (mg/L) of Cr (4.00, 2.00, 6.00) > Pb (25.00, 15.00, 10.00), > Ni (1.50, 1.00, 0.50) > Co (3.0, 2.0 , 1.00) are presented in table 1 and figure 8. The higher the concentration of heavy metals in the contaminated water, the higher the efficiency of the adsorbent (modified NPs) (El Awady et al., 2021). However, the efficiency decreases at lower concentration as shown in Ni (0.50) and Co (1.0). The results compared favorably with the one documented by El awady et al. (2021), in which modified green AgNPs were employed in the removal of zinc, chromium, lead and cadmium. Similarly, the outcome of this research work agrees with Ahmed et al. (2013) that there is high efficiency of absorption ability of modified NPs for removal of Pb, Cd and Cr. Furthermore, it has been revealed from literature that green modified NPs have the potential to accumulate at high bio-concentration factor of metals such as Zn, Pb, Ni, Cu and Cd (Ndeda, 2014 ; Bokhari et al., 2016). In addition, plant adaptivity shows the likelihood of the plant to adsorb the pollutants (Li et al., 2021; Branković et al., 2012).



Data are presented as mean ± SD of three replicates (n= 3). Superscripts "a, b, c, d & e" with different alphabets are significantly different at $p < 0.05$.
Pb (mg/L) : SA = 10.0; SB =15.0; SC = 25.0 and Co (mg/L) : SD = 1.0; SE = 2.0 ; SF = 3.0

Figure 9: The data analysis for Pb and Co.



Data are presented as mean ± SD of three replicates (n = 3). Superscripts "a, b, c, d" with different alphabets are significantly different at $p < 0.05$.
Cr (mg/L) : SG = 2.0 ; SH = 4.0; SI = 6.0 and Ni (mg/L): SJ = 0.5 ; SK = 1.0 ; SL = 1.5

Figure 10: The data analysis for Cr and Ni.

Data presented in mean and standard error of means of three replicates (n=3). Analysis were done using GraphPad Prism version 8.0.1 (244), GraphPad, Software, La Jolla California USA. One-way analysis of variance (ANOVA) was used to established the statistical significance. A *p*-value lower than 0.05 was considered to be statistical significant as represented in figure 9 and 10.

Conclusion

The silver nanoparticles (AgNPs) were produced with *S. birrea* stem bark extract and characterized with UV-Vis absorption spectrophotometer, SEM, EDS, XRD and TEM. The surface shape, composition, crystallinity and biogenic structure of the AgNPs were shown by SEM, EDS, XRD and TEM,respectively. Modified NPs of the extract conjugate presents high absorptional capacity of thePb, Co, Cr and Ni in the analyzed sample. The findings showed that the more the concentration of heavy metals presence in the contaminated water,the more the contaminants of interest were (Pb, Co, Cr and Ni) wereabsorbed by the absorbent, which were howevere reverse in terms of the absorptivity strength at alower concentration of the metals. The bark extract of *S. birrea*are stronglysuggested for its green synthesis(NPs) application in the waste management process of contaminated water owing to its

high yield and cleansing ability in the removal of heavy metal contaminants in waste water demonstrated in this study.

Conflicts of Interest: There is no conflict of interest among the authors.

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