Biosynthesis of Ag-Cu-Al Nanoparticles for Efficient Adsorption of Lead, Iron and Chromium from Industrial Wastewater

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ABSTRACT

Lack of proper effluent disposal methods in industries has led to an exacerbation of the risk posed by heavy metal contaminants present in industrial wastewater. Several approaches have been explored to mitigate these harmful threats but, most of these approaches have several limitations such as, lacking selectivity, removing essential ions along with heavy metals, high post-treatment cost and generating toxic byproducts which further contaminates the environment. To address these difficulties, nanoparticles have recently been employed to mitigate these limitations. Nanoparticles, owing to their minute size and large surface-to-volume ratio, exhibit enhanced reactivity and adsorption capacities, making them exceptional contenders for heavy metal removal. Furthermore, the synergistic effect of trimetallic nanoparticles has also increased its efficacy as an adsorbent. This study efficiently biosynthesized silver-copper-aluminum trimetallic nanoparticles (Ag-Cu-Al NPs) using aqueous leaves extract of Hierochloe odorata at room temperature. The synergistic effect of the three metals was efficiently harnessed in conjunction with the biologically active components from Hierochloe odorata present in the nanoparticles, to enhance the adsorption affinity of the nanoparticles towards available heavy metal ions present in the wastewater. The biosynthesized Ag-Cu-Al NPs was first confirmed by an obvious color shift from grey to olive green after adding the aqueous leaves extract to the trimetallic salt solution of silver nitrate, copper chloride and aluminum oxide. UV-vis spectroscopy of the nanoparticles presented a distinct peak maximum at 405 nm. The possible secondary metabolites responsible for bio-reduction, capping and homogeneity of the nanoparticles were assessed using FTIR. The crystalline nature and particle size of the NPs were investigated using XRD. SEM-EDS analysis revealed the surface texture and constituent elements of the NPs. Adsorption studies demonstrated that the biosynthesized Ag-Cu-Al nanoparticles acts as a highly efficient nano-adsorbent for the removal of lead, iron and chromium from industrial wastewater.

Keywords: Nanoparticles, Wastewater, Heavy metals, Biosynthesis, Hierochloe odorata, Adsorption.

INTRODUCTION

Burgeoning industrialization and urbanization have resulted in considerable health concerns as a result of indiscriminate wastewater discharge which introduces enormous amount of harmful heavy metals such as mercury, iron, lead, cadmium, arsenic, copper, zinc and nickel into water bodies. These poisonous metals constitute grave health challenges due to their toxic and carcinogenic effect [1]. The environmental impact of heavy metals in wastewater is extreme, causing disruptions to the ecosystem and endangering biological diversity. Heavy metals accrue in aquatic habitats through mining activities, industrial discharges and natural occurrences like weathering of rocks leading to contamination of surface water, groundwater, and sediments, where they exert toxic effects on flora and fauna. For instance, mercury bioaccumulates in fish through food chains, reaching concentrations that harm predatory species and human consumers [2]. Heavy metals have also been proven to degrade soil quality when contaminated wastewater is used for irrigation. Lead and cadmium alter microbial communities essential for nutrient cycling, reducing the soils inherent fertility and agricultural yields [3].

Unlike other biodegradable contaminants, heavy metal's non-biodegradable characteristics enhances their doggedness and increased concentration in the environment. This often leads to extensive and indefinite heavy metal pollution of the soil, water and the ecosystem [4]. When humans are exposed to heavy metals through contaminated food and water it can lead to acute health challenges ranging from nervous disorders to cancer, with susceptible groups like children and pregnant women facing increased risks [5]. In 2019, the World Health Organization (WHO) reported that an estimated 1 million people were killed as a result of exposure to lead exposure while approximately 140 million people from 70 countries have been exposed to arsenic contaminated drinking water [6,7].

Industrial effluent from deserted mining sites and other industrial activities is usually characterized by various heavy metals, Pb, Cu, Cd, Cr, Ni and Mn. These pollutants constitute a great risk to the biota, resulting in a range of diseases and dysfunction. For example, exposure to lead (Pb) has been linked with cardiovascular issues, kidney damage, hyperactivity, mental retardation, and dermatitis. Conversely, susceptiveness to Chromium has been linked with the development of acute respiratory issues, skin disorders, kidney failure, and enfeebled immune systems [8]. The acceptable concentration of lead (II) and Chromium (VI) ion in drinking water by World Health Organization (WHO) is 0.05 mg/L [9]. Also, the presence of these contaminants can contribute to the development of skin exfoliation, disruption of thyroid function, development of liver cirrhosis and gastrointestinal issues such as death of organisms, stalled growth, diarrhea and reduced reproductive rate [10, 11]. Therefore, the need to immediately implement efficient treatment methods for industrial wastewater and prevent its release into the environment and alleviate these detrimental consequences cannot be overemphasized.

Customary methods employed for heavy metal remediation from industrial wastewater, such as chemical precipitation, coagulation-flocculation, ion exchange, membrane filtration, and reverse osmosis amongst others, have limitations that hinders their effectiveness. These methods often lack selectivity, removing essential ions along with heavy metals, high post-treatment cost and generating toxic byproducts like sludge [12]. For example, coagulation-flocculation processes result in the generation of high quantities of chemical sludge and can leave residual coagulant metals in the treated water among other [13]. Furthermore, conventional methods of heavy metal treatment can be very expensive and difficult to scale-up for large-scale industrial effluent treatment applications. For instance, graphene-based materials such as activated carbon are produced consequent upon high heat and pressure requirements, which are energy consuming and expensive [2, 12]. To address these difficulties, nanomaterial-based routes have emerged as encouraging solutions due to their distinct properties and diverse applications in heavy metal remediation [14].

Nanoparticles, owing to their minute size and large surface-to-volume ratio, exhibit enhanced reactivity and adsorption capacities, making them exceptional contenders for heavy metal removal [15]. Several research have shown that nanomaterials as well possess notable redox and catalytic properties. Their large surface area provides several active sites for interaction with heavy metal ions, expediting efficient adsorption and modification processes. Additionally, the tunability of nanomaterials allows for the alteration of their properties to target specific contaminants [16]. The tunability of these nanomaterials enhances their versatility in various environmental conditions. The potential for functionalization with specific ligands or coatings further enhances their astuteness and effectiveness in intricate environments. Nanoparticles are progressively traversed for environmental cleanup and sustainable effluent treatment technologies [17].

There are various types of nanoparticles depending on their size, morphology and other characteristics.
Metallic oxide nanoparticles such as silicon oxide nanoparticles, zinc oxide, tungsten oxide, magnesium oxide and titanium dioxide have been widely recognized for their potential in environmental remediation [18, 19]. Metallic nanoparticles have garnered significant attention among the numerous types of nanoparticles due to their exceptional stability in thermal and biological processes, photochemical effective adsorption capabilities, low toxicity and affordability [20]. When compared to monometallic nanoparticles, multi-metallic (trimetallic) nanoparticles, composed of various metals, provide a unified system that can display unique features. They exhibit enhanced catalytic activity and antibacterial effect, diversified shapes, high selective detection and sensitivity, high level of stability, and chemical transformation [21]. These enhanced characteristics are consequent upon the synergistic effects of the three metals that makes up the trimetallic nanoparticles [22].

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Different synthesis methods have been investigated for the synthesis of trimetallic nanomaterials but, the biogenic synthesis route has proven to be most affordable and environmentally friendly. This method involves the reduction of metal ions by biological entities to form nanoparticles. Distinct plants, microbes, and compostable wastes have been employed as starting materials in the synthesis of these nanoparticles via this route. Green plant constituents can be employed in this synthesis method due to phytochemicals present in plants, which serves as reductant, organic ligands, and stabilizers due to the presence of biologically active compounds such as hydroxylated polyphenols, isoprenoids, enzymes, and other free radical scavengers [23]. One of such plants that have been used in the synthesis of trimetallic nanoparticles is Hierochloe odorata. Hierochloe odorata (Also known as sweet grass) is an aromatic herb native to North America. It is used ceremonially through burning the dried and braided grass stems for an incense or smudge. Its distinctive sweet scent is associated to the presence of some natural aromatic organic chemical and is also rich in antioxidant [24].

This work aimed to investigate the biogenic synthesis of Ag-Cu-Al trimetallic nanoparticles using aqueous leaves extracts of Hierochloe odorata, characterization of the biosynthesized trimetallic nanoparticles using spectroscopic and microscopic techniques, and to investigate its possible application in the removal of heavy metals Lead (Pb), Iron (Fe) and Chromium (Cr) from simulated wastewater solution. The aqueous leaves extract of the plant used serves as reductant, organic ligands, and stabilizers due to the presence of diverse secondary metabolites present in the extract. There has been no previous report of the use of biosynthesized AgCu-Al trimetallic nanoparticles in heavy metal removal hence, this study intends to harness the synergistic effect of the trimetallic nanoparticles coupled with the biologically active components from Hierochloe odorata present in the nanoparticles in order to enhance the adsorption affinity of the nanoparticles towards available heavy metal ions present in the aqueous solution of the wastewater [25, 26].

MATERIALS AND METHODS

Materials and Chemicals

The plant materials used was Hierochloe odorata leaves collected from the Federal College of Forestry Jos, Nigeria and identified by a plant taxonomist. The chemicals used were analytical grade copper (II) chloride ($CuCl_2$), silver nitrate ($AgNO_3$), aluminum oxide (Al_2O_3), Iron (II) Chloride ($FeCl_2$), Potassium dichromate ($K_2Cr_2O_7$), Lead acetate ($Pb(C_2H_3O_2)_2$), and obtained from Thermo Fisher Scientific Pittsburgh, PA, United States of America. The chemical compounds and substances were used as received without further refinement or alteration.

METHODS

Preparation of Aqueous leaves extract of Hierochloe odorata

Accurately weighed 10 grammes of fresh Hierochloe odorata leaves was washed with running tap water and rinsed with distilled water for removal of dust particles. Subsequently, the leaves were cut into pieces, weighed and transferred into a 500 mL beaker containing 100 mL of distilled water and then placed on a hotplate for 15 minutes at 30ºC after which it was allowed to cool and then filtered using Whatman filter paper No. 1.
The filtrate was then kept for subsequent use.

Preparation of 0.1 M $AgNO_3$, $CuCl_2$, and Al_2O_3 Salt Solutions

Exactly 1.70 g, 1.34 g and 1.02 g of silver nitrate, copper (II) chloride and aluminum oxide salts respectively were weighed and transferred into three beakers containing 100 mL each of demineralized water. The resultant mix were properly agitated to ensure the salt dissolves properly after which the salt solutions were mixed together to obtain a homogenous mixture. The prepared salt solutions were then stored for subsequent use **2.2.3 Biosynthesis of Ag-Cu-Al Trimetallic Nanoparticles**

Ag-Cu-Al trimetallic nanoparticles was successfully biosynthesized by bio-reducing the stock solution of silver, copper and aluminum salts concurrently with the aqueous leaves extract. 30 mL of the leaf extract was added to

150 mL of 0.1 M $AgNO_3$-$CuCl_2$-Al_2O_3 stock solution (50 ml of each salt solution) in dropwise manner with continuous stirring on a magnetic stirrer. After a little while, a colour change was observed indicating the formation of the trimetallic nanoparticles. The nanoparticles formed was centrifuged at 3000 rpm for 15 minutes, after which it was washed with distilled water and allowed to dry at room temperature. It was then set aside for onward use.

Characterization

The biosynthesized trimetallic nanoparticles was put through certain spectroscopic and microscopic characterization methods to determine the size, morphology and composition of the biosynthesized nanoparticles. UV-Visible spectroscopic measurements of the biosynthesized nanoparticles were analyzed using the T70 PG Instruments' UV- Spectrophotometer. The possible secondary metabolites present in the plant extract responsible for the bio-reduction of the trimetallic salt solution were determined using FTIR spectrophotometer (Cary 630 Agilent Technologies). SEM–EDS analysis was recorded using Quanta 250 FEG instrument to investigate the surface morphology and elemental composition of the nanoparticles. The crystal lattice and size distribution of the biosynthesized nanoparticles was analyzed using X-ray diffraction (XRD Empyrean Malvern Panalytical diffractometer).

Applications

Heavy Metal Adsorption Studies

Exactly 1.27 g, 2.94 g and 3.25 g of $FeCl_2$, $K_2Cr_2O_7$, and $Pb(C_2H_3O_2)_2$ respectively were weighed and transferred into separate beakers containing 100 ml each of deionized water in order to prepare 0.1 M solutions of the various metal salts. Adsorption studies were carried out by mixing 2, 4, 6, 8 and 10 mg of biosynthesized silver-copper-aluminum trimetallic nanoparticles (Al-Ag-Cu TMNPs) with 5 ml each of 0.1 M $FeCl_2$, $K_2Cr_2O_7$ and $Pb(C_2H_3O_2)_2$ Solutions (Simulated waste water). The solutions were then placed in an ultrasonic bath to ensure that the nanoparticles dissolved properly in the test solution.

Atomic Absorption spectrophotometer (AAS) was used to analyze the concentration of the metal ion present in the simulated waste water, with and without the biosynthesized trimetallic nanoparticles. The amount of metal ion absorbed by the adsorbent (nanoparticles) was evaluated and percentage removal calculated as;

$$\% \text{ Removal} = [(C_0 - C_e) / C_0] \times 100 \quad (1)$$

Where Co and Ce are the initial and final concentration of the pollutant (simulated waste water)

RESULTS AND DISCUSSION

Optical Properties

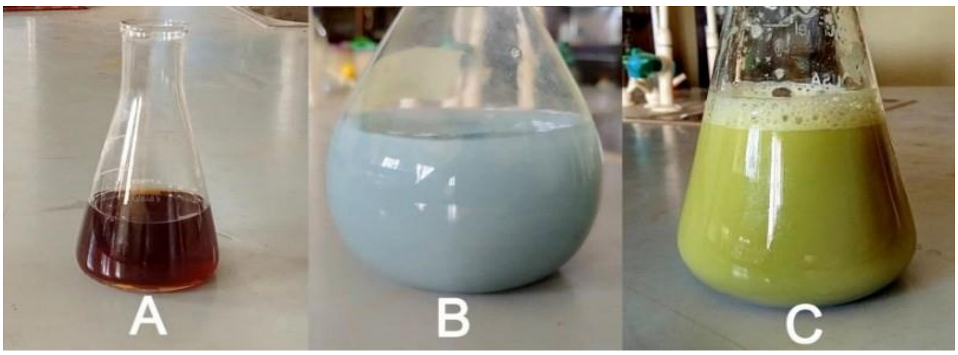

Plate 1: Hierochloe odorata leaves extract (A), Ag-Cu-Al trimetallic salt solution (B), Ag-Cu-Al nanoparticle solution (C)

One unique attribute of nanoparticles is their opto-electronic properties. The opto-electronic property of the trimetallic salt solution of Ag-Cu-Al, Hierochloe odorata leaf extracts and the trimetallic nanoparticles of Ag-

Cu-Al are shown on plate 1. After addition of 30 ml of aqueous leaf extract of Hierochloe odorata the colour of the 150 mL of the 0.1 M trimetallic salt solution of Ag-Cu-Al changed from grey to olive green indicating the formation of Ag-Cu-Al trimetallic nanoparticles. The excitation of the surface plasmon resonance action in the nanoparticles is responsible for the colour variations. The size and shape of metal surface plasmon oscillation, as well as their optical properties are well understood.

UV-Visible Spectroscopy Analysis

More information about the biosynthesized Ag-Cu-Al trimetallic nanoparticles was obtained through the use of Ultraviolet-visible spectroscopy, which aided in observing the bio-reduction of hydrated metal ions on addition of the aqueous leaves extract (figure 1). In the absorption spectrum of Ag-Cu-Al trimetallic nanoparticle, the characteristic surface plasmon resonance (SPR) is observed with an absorbance of approximately 400-407 nm with peak maximum of 405 nm, which can be attributed to the presence of Ag-Cu-Al trimetallic nanoparticles. The nearly ordered structure of the collective electron oscillation suggest that the nanoparticles are not evenly spread and homogenous. This heterogeneity of the nanoparticles is responsible for the extensive absorption band. The size, shape and stabilizing agent of nanoparticles influence the location of the SPR band.

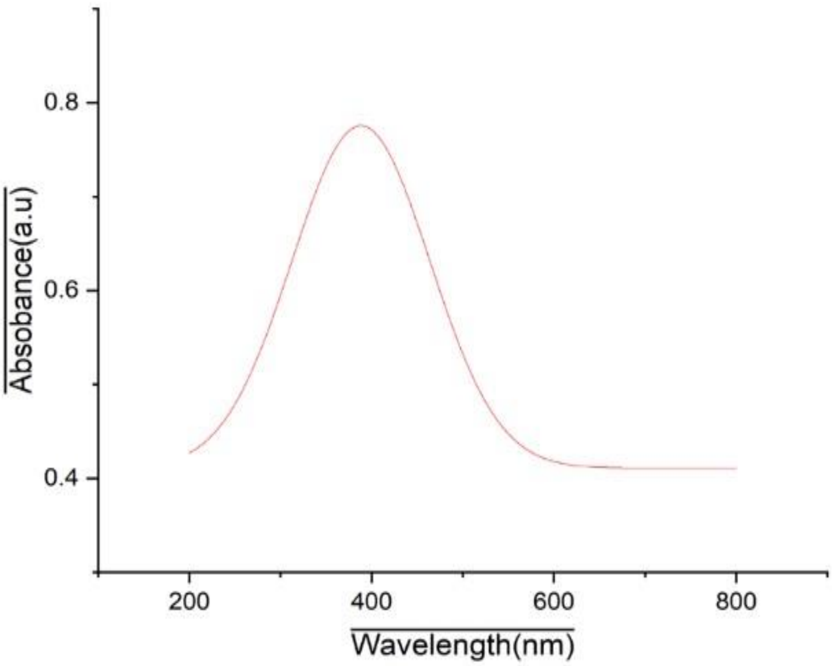

Figure 1: Ultraviolet-Visible Spectrum of Ag-Cu-Al trimetallic nanoparticle

Fourier Transform Infra-Red Spectroscopy Analysis

Figure 2 shows the FTIR spectra of Hierochloe odorata aqueous leaf extract mediated synthesized AgCu-Al trimetallic nanoparticles. It shows the distinct absorption bands for the functional groups responsible for the reduction of the trimetallic ions. Spectral peaks were obtained at 3317, 2938, 2080, 1735, 1367, 1217 and 1033 cm^{-1}. The spectral lines at 3317 cm^{-1} corresponds to secondary amine (N-H), C-H medium stretching for alkane is responsible for the bonds found 2938 cm^{-1}. The 2080 cm^{-1} stems from C=C stretch for alkenes, 1735 cm^{-1}. IR band is associated with C=O stretching for esters. 1367 cm^{-1} is strong band for N=O stretching for nitro compounds While 1217 cm^{-1} is attributed for C-O stretch for esters and 1033 cm^{-1} is for C-C bending stretch for alkanes. Hierochloe odorata leaves extract is rich in secondary metabolites such as polyphenols, alkaloids and hydrates of carbon, saponins and flavonoids which are rich in free radical scavengers efficient in contributing atoms of hydrogen and protein components that are capable of attaching themselves with metallic ions and efficient in reducing metal ions of silver, copper and aluminum and also serve as stabilizers to the synthesized nanoparticles [27].

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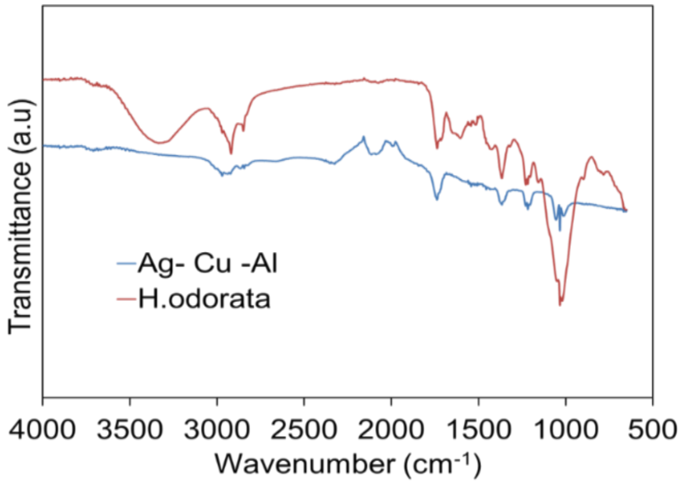

Figure 2: Comparative FTIR spectra of Ag-Cu-Al nanoparticles

XRD Analysis

The X-ray diffraction pattern is used to determine the size, shape, fragment examination and specification of the sample. The location of the peaks obtained from spectral markings also gives details about the magnitude and shape of the crystal. The medium size of the Ag-Cu-Al nanoparticles was calculated using the DebyeScherrer equation;

$$D = \frac{K\lambda}{\beta\cos\theta}$$

where; D, is the size of the crystal, k = constant (0.94), ƛ = wavelength of incident rays βcosθ on the crystal (1.5418 Å), β= is the width at half maxima at (111) reflection at Bragg's angle 2θ, while θ is the Bragg angle.

From the XRD patterns of the biosynthesized Ag-Cu-Al nanoparticles as depicted in Figure 3, it is clear that the diffraction pattern of the trimetallic nanoparticles were essentially crystalline as observed with the sharp peaks. Predicted Bragg peaks observed at 38.47°, 44.67°, 47.12° and 65.23° corresponds to the (111), (200) and (220) standard face centered cubic structures of silver which establishes the presence of silver oxide in the sample [28, 29]. Diffraction peaks were also observed for copper oxide at 28.85° and 33.26°, aluminum oxide at 57.75° and 58.60° brought about by the oxidation of copper and aluminum particles respectively [30]. The average particle size of the biosynthesized Ag-Cu-Al trimetallic nanoparticles was computed from table 1 to be 35.92 nm. The values of the crystal planes of the biosynthesized Ag-Cu-Al nanoparticle observed were consistent with the standard powder and diffraction card of Joint Committee on Powder Diffraction Standards (JCPDS) which revealed that the trimetallic Ag-Cu-AL nanoparticles exhibit's a Face center cubic crystal. Other diffraction peaks observed in the spectrum might be from some biomolecules or proteins within the plant extract [31].

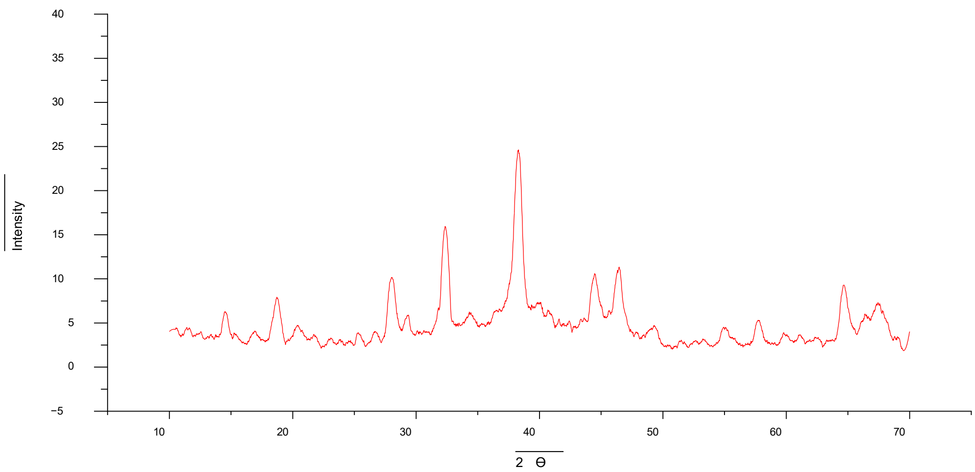

Figure 3: Xray Diffraction spectrum of Ag-Cu-Al nanoparticles

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Table 1: Particle size of Ag-Cu-Al Trimetallic nanoparticles

Table: XRD Peak Parameters

Position (nm)	Height (Abs)	FWHM (radians)	d-Spacing (Å)	Particle Size (nm)
15.195	6.103	0.725	0.173	9.275
19.157	8.234	0.636	0.137	21.977
29.781	9.890	0.720	0.317	32.955
33.292	15.106	0.210	0.278	39.677
38.789	23.207	0.265	0.387	45.012
45.016	11.026	0.425	0.167	51.072
47.129	11.221	0.328	0.241	55.596
57.321	4.476	0.352	0.195	63.047
65.230	9.652	0.346	0.268	67.786

SEM-EDS Analysis

This characterization method was used to determine the surface configuration of the Ag-Cu-Al nanoparticles as depicted in plate 2 below. The surface conformation revealed an irregular crystalline structure which is synonymous of metallic nanocomposites due to the strong intermolecular contact imposed by the high surface energy. It also reveals the complexity of the particle size to be closely packed and also the cylindrical nature of the nanoparticles. The image also shows a coarseness which might be ascribed to organic molecules present in the leaf extract that are bounded to the Ag-Cu-Al nanoparticles. The EDS also revealed the elemental composition of the nanoparticles with silver which is easily displaced and hence more active and having the highest composition thereby forming the outer shell while aluminum forms the inner core shell.

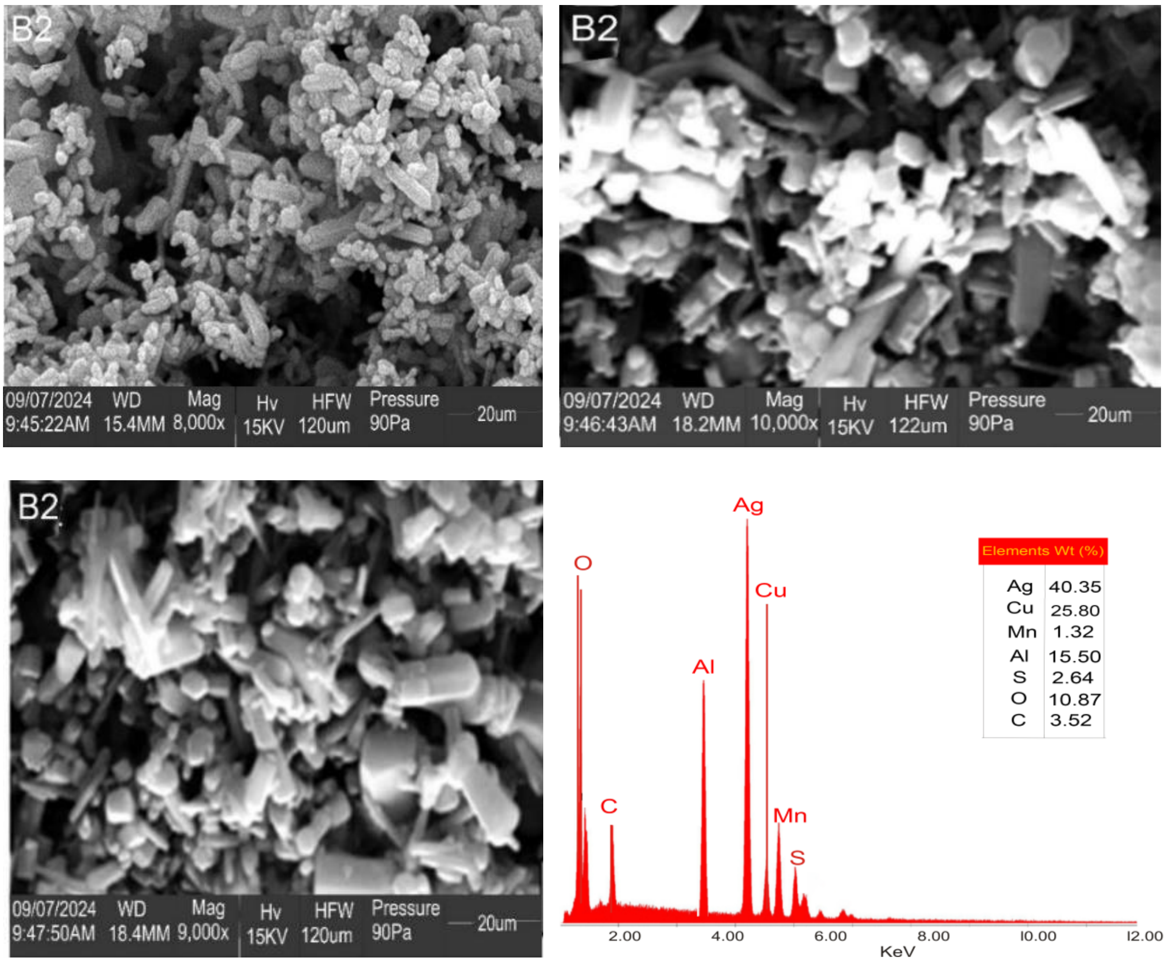

Plate 2: SEM-EDS images of Ag-Cu-Al nanoparticles

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Adsorption studies of Ag-Cu-Al Trimetallic Nanoparticles

Adsorption has been proven to be one of the most widely applied techniques in wastewater treatment due to its simplicity, cost-effectiveness, and high efficiency in removing heavy metals and other toxic contaminants from aqueous media [32]. Unlike precipitation, ion exchange, or membrane filtration, adsorption does not generate excessive secondary pollutants, making it an environmentally sustainable approach for water purification. The technique relies on the interaction between the adsorbate molecules or ions and the active sites available on the surface of the adsorbent material [33]

Metallic nanoparticles such as Ag–Cu–Al trimetallic nanoparticles present a promising adsorbent candidate for the removal of these heavy metals due to their synergistic properties of high stability, antimicrobial activity, and enhanced surface functionality [34]. The presence of silver contributes a high surface area and energy, copper enhances electron transfer and adsorption kinetics, while aluminum improves stability and provides additional active sites for complexation [35]. Investigating the adsorption behavior of Pb, Fe and Cr ions using biosynthesized Ag–Cu–Al trimetallic nanoparticles will provide valuable insights into their adsorption capacity, efficiency, and underlying mechanisms, ultimately establishing their potential application in wastewater treatment. The results of the adsorption studies conducted for the removal of Lead (Pb), Iron (Fe) and chromium (Cr) from waste water using biosynthesized Ag-Cu-Al Trimetallic nanoparticles as adsorbent are presented below;

Table 2. Results of Adsorption studies of Al-Cu-Ag Trimetallic nanoparticles on Lead (Pb)

Ag-Cu-Al Concentration (ppm)	Pb Concentration (mg/L)	% Removal
Blank	16.39 ±0.008	0
50	9.098 ±0.002	44.52
100	8.979 ±0.004	45.25
150	5.925 ±0.002	63.87
200	1.207 ±0.005	92.64
250	1.067 ±0.009	93.49

The results in table 2 shows a progressive decrease in lead (Pb) concentration with increasing concentrations of Ag–Cu–Al nanoparticles with optimum percentage removal of 93.49 % obtained at 250 ppm. A positive correlation between adsorbent concentration and removal efficiency was observed and is a well-established principle in adsorption science, as a higher mass of adsorbent provides a greater surface area and more active sites for metal ion binding [36].

The exceptionally high efficiencies (above 93 %) at higher concentrations highlight the strong adsorption affinity and capacity of the synthesized trimetallic nanoparticles for lead ions. The high effectiveness for lead (Pb^{2+}) removal is typical of nanoscale adsorbents, which exhibit strong complexation with heavy metal cations [37]. This performance is attributed to the high surface area and the synergistic effects of the Ag-Cu-Al composition, which provide abundant active sites for metal ion binding. The organic capping agents from the *Hierochloe odorata* aqueous leaf extract containing phenolic and carboxyl groups, further enhance this capacity by facilitating metal ion complexation [38]. Although some variability in measurement precision was observed, the steady and sizeable decline in residual lead concentration across all concentration confirms the reliability and effectiveness of the treatment method for lead-contaminated wastewater.

Table 3. Results of Adsorption Studies of Al-Cu-Ag Trimetallic nanoparticles on Iron (Fe)

Ag-Cu-Al Concentration (ppm)	Pb Concentration (mg/L)	% Removal
Blank	19.343 ±0.001	0
50	8.220 ±0.007	57.51
100	6.841 ±0.005	64.64
150	4.173 ±0.001	78.43

200	1.984 ±0.004	89.74
250	1.046 ±0.006	94.59

The results in table 3 shows a progressive decrease in iron (Fe) concentration with increasing concentrations of Ag–Cu–Al nanoparticles. It also reveals a clear increasing trend in removal efficiency, rising from 57.51% in 50-ppm to 94.59 % in 250-ppm. The exceptionally high efficiencies at higher dosages highlight the strong adsorption affinity of the synthesized nanoparticles for iron ions. The high removal capacity for iron is consistent with literature showing that metal oxide-based nanomaterials, particularly those containing aluminum, exhibit high affinity for Fe ions through surface complexation and electrostatic interactions [39]. This performance is attributed to the synergistic effects of the Ag-Cu-Al composition. The presence of aluminum is particularly strategic, as it provides hydroxyl groups that facilitate ligand exchange and binding of iron species [40]. Furthermore, the organic capping agents from the *Hierochloe odorata* aqueous leaf extract provide additional functional groups (e.g., carboxyl, phenolic) that enhance adsorption through complexation and hydrogen bonding [38]. The consistent and substantial decline in residual iron concentration confirms the effectiveness of the nanoparticles for iron-contaminated wastewater treatment.

Table 4: Results for Adsorption studies of Al-Cu-Ag Trimetallic nanoparticles on Chromium (Cr)

Ag-Cu-Al Concentration (ppm)	**Pb Concentration (mg/L)**	**% Removal**
Blank	13.05 ±0.009	0
50	9.097 ±0.005	30.04
100	7.114 ±0.007	45.29
150	6.863 ±0.003	47.22
200	6.612 ±0.006	52.23
250	4.876 ±0.002	62.50

From the results obtained, a progressive decrease in chromium (Cr) concentration with increasing concentrations of Ag–Cu–Al nanoparticles were observed as shown in table 4. Removal efficiencies were observed to progressively increase from 30.04 % at 50-ppm, to 62.50% for 250-ppm. This positive correlation between adsorbent dosage and removal percentage is a well-established principle in adsorption science, as increased nanoparticle mass provides a greater abundance of active surface sites for metal binding [41]. The measurable efficiencies confirm the adsorption capability of the synthesized nanoparticles for chromium ions.

However, the overall lower and gradual increase in removal efficiency, compared to lead and iron, suggests a weaker affinity or less optimal adsorption conditions for chromium species. This is likely because chromium (VI) primarily exists as oxyanions (e.g., $HCrO_4^-$, CrO_4^{2-}) in aqueous solutions, which can experience electrostatic repulsion with the potentially negatively charged surface of the nanoparticles at neutral pH [41]. The organic capping agents from the *H. odorata* extract may also be more effective at complexing cationic metals like Pb^{2+} and Fe^{3+} than anionic chromium species [38]. The consistent reduction in residual concentration, nonetheless, confirms the effectiveness of the Ag-Cu-Al nanoparticles for chromium uptake, indicating that mechanisms such as reduction or electrostatic attraction despite repulsion may be contributing to the removal process [42].

CONCLUSION

This study successfully demonstrated the biogenic synthesis of silver-copper-aluminum (Ag-Cu-Al) trimetallic nanoparticles (TMNPs) using aqueous leaf extract of Hierochloe odorata and evaluated its efficacy in adsorbing heavy metals from wastewater. The biosynthesis and properties of the nanoparticles were confirmed using UV-Vis spectroscopy, FTIR, XRD, and SEM-EDS techniques, which verified its crystalline nature, irregular coarse surface conformation, elemental composition, and cylindrical morphology. Adsorption studies demonstrated that the biosynthesized Ag-Cu-Al nanoparticles acts as a highly effective nano-adsorbent for the removal of heavy metals from aqueous solution. This is attributed to the synergistic effect of the three metals coupled with the organic capping agent present the nanoparticles which enhances active sites for complexation. The results showed that the removal efficiency increased significantly with higher adsorbent (nanoparticle) dosage. The nanoparticles exhibited a strong and preferential affinity for different metals, with the maximum removal efficiencies recorded at 94.59% for Iron, 93.49% for Lead, and 62.50% for Chromium. This establishes Hierochloe odorata-mediated synthesized Ag-Cu-Al trimetallic nanoparticles as a promising, environmentally friendly, and efficient material for wastewater remediation, particularly for the extraction of toxic heavy metals like lead, iron and chromium from contaminated environments. The eco-friendly synthesis route employed and the minute (nanosized) quantity of the trimetallic nanoparticles used in heavy metal remediation from wastewater in this study can help in allaying/reducing the concerns of toxicity and long-term effects of nanoparticles on the environment

Conflict Of Interests

Authors have declared that no conflict of interest exist.

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