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Green Synthesis of Silver Nanoparticles(AgNPs) using *Calotropis procera* Leaves Extract and it Adsorption Properties for the Removal of Cr^{3+} from Petroleum Waste Water

Kantoma, D., [1*] Nwokem,C.O.,[2] Zaradeen N.Garba. [3] James Yusuf

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Abstract: *In this research work, silver nanoparticles (AgNPs) were synthesized using calotropis procera leaf extract. The Fourier Transformed Infrared (FT-IR) result of calotropis procera shows functional groups that are capable of reduction and stabilization of the AgNPs nanoparticles such as alcohols which is suitable for the synthesis of AgNPs. The produced nano adsorbent was characterized using X-ray powder diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR) and energy dispersive infrared(EDX). The SEM micrographs revealed well-dispersed silver nanoparticles (AgNPs) and the XRD showed a crystalline nanoparticle. The FT-IR shows a carbon stretched region signifying aldehydes while EDX shows that carbon and hydrogen have higher percentage concentrations which depict carbonated and hydrolysed AgNPs. Percentage removal of chromium was 97.58% at the highest dose of 1.0g.*

Keywords: Toxicity, heavy metal, remediation, water, separation technology, nanoparticles *Heavy metal, Nanoparticles, silver nanparticles; Oil refinery wastewater*

Kantoma, D.,
Department of Applied Chemistry, Kaduna Polytechnic Kaduna, Nigeria
Email: kantomadogara@gmail.com,
Orcid id:

Nwokem, C. O
Department of pure and Applied Chemistry, Kaduna State University, Nigeria
Email:
Orcid id:

Zaradeen N.Garba.
Department of Chemistry, Ahmadu Bello University Zaria, Nigeria, Kaduna State, Nigeria
Email:
Orcid id:

James Yusuf
Department of Applied Chemistry, Kaduna Polytechnic Kaduna, Nigeria
Email:
Orcid id:

1.0 Introduction

Drinking water is one of the most important and necessary elements to life on earth it is derived from a variety of sources depending on local availability; such as surface water (rivers, lakes, reservoirs and ponds), groundwater (aquifers) and rainwater. These sources vary in terms of contaminant risk (Dave *et al.*, 2002). The pollution of water resources due to the disposal of contaminants has been an increasing worldwide concern for the last few decades. The most common water pollutants are inorganic and organic matter. They are discharged into the water by natural phenomena or human activities ranging from discharge of effluents from municipal waste or industrial activities such as petroleum refining. Chemicals that are discharged into the surface and subsurface waters from these effluents are causing problem problems to the environment. The adverse effect of untreated wastewater on the environment has necessitated the governments of most countries to impose stringent legislation for the treatment of industrial wastewater before disposal to avoid both acute and chronic toxicities (Dey and Islam, 2015). The growth in the refining of oil refinery products has increased the release of pollutants such as lead, Chromium, sulphide, and phosphate, among others into the ecosystem in Nigeria.

Recently, nanomaterials are considered as good materials for wastewater treatments (Shannon *et al.*,2008). Since the last decade, the most effectively studied nanoparticles are those made from noble metals such as silver, gold and platinum. Due to excellent physicochemical properties, nanoparticles have potential applications in all fields of science and technology. Recent studies revealed that AgNPs can attach to heavy metals such as chromium and and remove it from wastewater by adsorption. AgNPs are widely used in biology, wastewater treatment and medicine especially because of their attractive and unique physiochemical properties (Haiza *et al* .,2013). However, adsorption is an effective and friendly method for removing both organic and inorganic pollutants from wastewater. this solves the problem of sludge disposal(Ovasif *et al.*,2013) Therefore this paper, aims to study the potential of silver nanoparticles via the green synthesis method.

2.0 Materials and Methods

2.1 Materials

Plant samples of Roster tree (giant milkweed or Sodom apple) (Tumfafiya in Hausa) Leaves extract (*Calotropis Procera (Ait)*) were collected within Kaduna Polytechnic main campus Tudun-Wada Kaduna South Local Government Area Kaduna State- Nigeria. Its botanical identity was further confirmed and authenticated at the Herbarium section of the Department of Botany, Ahmadu Bello University Zaria, Nigeria. Voucher specimen number: V/N-ABU 0980219, English name: Giant Milkweed, Botanical name: *Calotropis Procera*, Family name: Asclepidaceae, Local name: Tumfafiya, Determinant: Namadi Sanusi, and was preserved and stored at the Herbarium for future reference.

2.2 Sample Collection

Collection and Characterization of the Refinery Wastewater (RWW)

The RWW used in this study was collected from Kaduna Refinery and Petrochemical Company (KRPC) in Kaduna state, Nigeria. The wastewater was analyzed for physicochemical parameters based on the recommendation of standard methods of water and wastewater analysis at the Federal Ministry of Agriculture Goning Gora and Water Resources Department Ahmadu Bello University, Zaria respectively in Kaduna state, Nigeria. The heavy metals were also determined using Atomic absorption spectroscopy (AAS).

2.3 Green synthesis of silver nanoparticles(AgNPs)

2.3.1 Preparation of metal precursor

This was done by dissolving 3.3963 g of $AgNO_3$ (99% M&B) in 1L of distilled water to prepare 0.02M silver nitrate solution.

2.3.2 Preparation of aqueous leaf extract

The flower leaves were collected and washed thoroughly under running tap water and rinsed severally with distilled water followed by air drying to remove residual moisture. The dried materials were cut into fine pieces and dispersed in 200 ml of sterile distilled water in a 500 ml glass beaker and boiled at 80^{o}C for 15 minutes and allowed to cool, then filter the solution thoroughly with Whatman no:1 filter paper (spring field mill. Maidstone .kent. England) and the filtrate was then used immediately for the synthesis silver nanoparticles.

2.3.3 Synthesis of silver nanoparticles

Silver nitrate ($AgNO_3$) salt was used as received without further purification. 5ml *Calotropis procera* leaves broth was added to 45 of 0.02M silver nitrate solution for the bioreduction process and allowed to react at ambient conditions (Haleemkhan *et al*., 2015). The observed colour change of the reaction mixture from transparent yellow to dark brown indicates the formation of Silver nanoparticles (Kulkarni *et al*., 2014). The suspension of Silver nanoparticles was allowed to settle and the excess liquid was removed. The particles were then rinsed to remove any organic residue and re-suspended in 95% ethanol for further characterization (Kasthuri *et al*.,2009).

Fig: 1 (a) *Calotropis procera* leaves before crushing (b) Crushed *Calotropis procera* leaves

2.4 Batch adsorption experiment

Batch adsorption experiment for the removal of chromium was carried out by agitating (0.2 to 1.0g) of the nanoparticles with 40cm^3 of the refinery wastewater in a 100cm^3 Erlenmeyer flask at constant temperature (20^{o}C to 60^{o}C) and at 300 rpm. The mixture was then centrifuged for 10 minutes at 3000 rpm and the supernatant was used for spectrophotometric analyses. The final concentration of the wastewater after agitation was determined and the effects of agitation time (10 to 60 minutes), adsorbent dose (0.2 to 1.0g), and temperature (20^{o}C to 60^{o}C) on the adsorptive removal of the chromium in wastewater was investigated. The percentage of chromium in wastewater removal (%R) was calculated using equation 1 (Eddy *et al*., 2024a))

$$\%R = \frac{C_0 - C_e}{C_0} \times \frac{100}{1} \qquad (1)$$

where C_o and C_e are the initial and concentrations (mg/L) of Chromium initially. (Ibrahim and Abdullahi, 2017). The experimental data obtained were used to investigate the potential of AgNPs on refinery wastewater.

3.0 Results and Discussion

3.*1* *Characterization study*

The FTIR spectrum of *calotropis procera* leaf-mediated AgNPs is shown in Fig.2 while the functional groups identified and assigned to the peaks are shown in Table.1 concerning the corresponding absorption peaks Major peaks observed in the spectrum (Table 1) were due to C-N, C-H, C-O, C-O, C=O and C − C ≡ C−H stretches as shown in Table 1 These vibrations are due to the phytochemicals in the plant leaf extract. The displayed functional groups in Table 1 are a direct signal of the existence of phytochemicals such as alkaloids, phenol, etc.

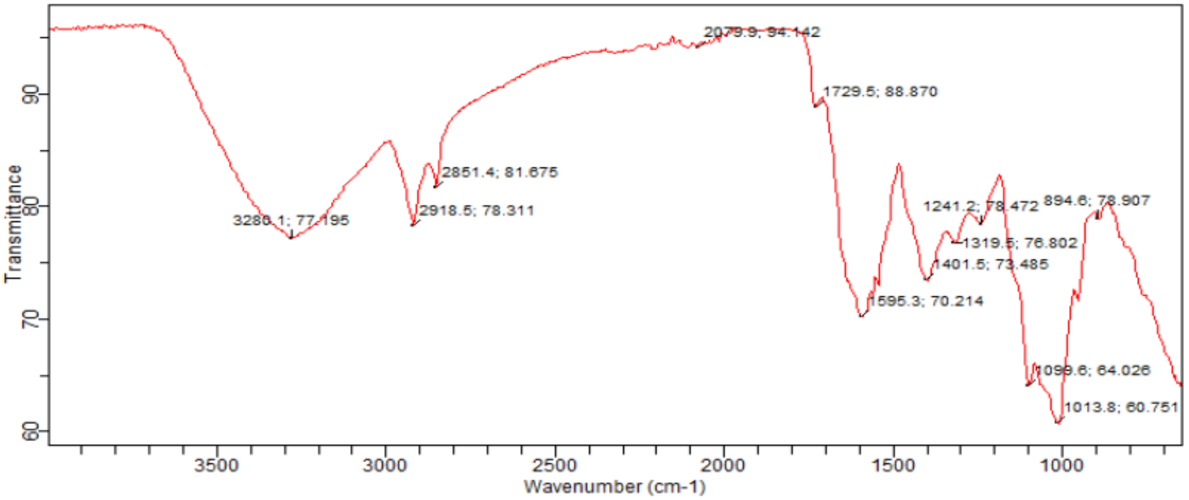

Fig.2: FT-IR of *calotropis procera* leave.

Table 1: Results of the FT-IR Spectroscopy for *calotropis procera* leaf

Wavelength (cm^{-1})	**Vibration**	**Assignment**
1014	C=N stretch	Aliphatic amines
1100	C=N stretch	Aliphatic amines
1895	C-H imp	Aromatics
1241	C-C stretch	Alcohols, ester
1320	C-O stretch	alkanes
1595	C-H stretch	aromatic
1730	C-O stretch	α,β unsaturated,ester
2851	C-H stretch	Alkanes
2919	C-H stretch	Alkanes
3280	C − C ≡ C−H:C−H stretch	Alkyne

Fig. 2 and Table 1 depict some of the functional groups that are responsible for the reduction and stabilization of the AgNPs.

To identify the vibrational pattern that is native to the synthesised AgNPs, the FTIR of the product was also taken and is shown in Fig. 3. The vibration peaks assigned to the identified peaks (Table 2) reveal an increase in the number of peaks compared to those observed in the plant extract.

Fig. 4 shows the XRD pattern of the synthesised nanoparticles showing a principal peak at about [2Theta] = 39 ° while other peaks were found at 36, 45 and 65 °. The observed principal peaks is in a position that is consistent with some literature values. For example, AgNPs synthesised from an aqueous extract of *Echinochloa pyramidalis* by Akpanudo and Olabemiwo (2024a) showed a principal peak at {2Theta] = 43 °. However, in their work, several peaks were observed and were attributed to the capping of the phytochemicals. In this study, only four peaks are observed which suggests that the reduction of the silver salt by the phytochemicals in the used plant is much better.

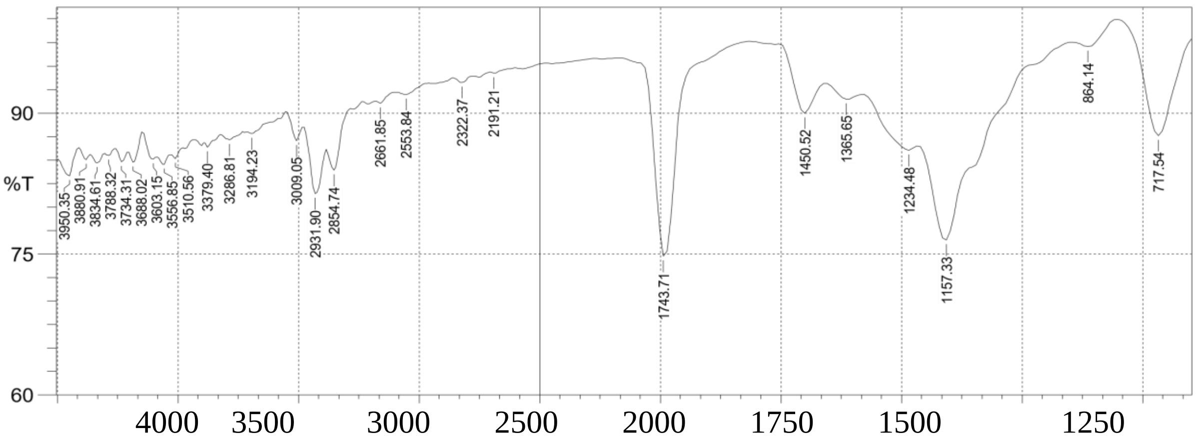

Fig. 3: FTIR spectrum of silver nanoparticle

Table 2: Results of FT-IR Spectroscopy of Synthesized AgNPS

Peaks (cm^{-1})	Bond	Functional groups
3566.85 Above	O – H	Hydroxyl group, lipids
3510.56	O – H	Alcohol
3379.40	N – H stretch	1^0 Amine
3286.81	C ≡ C – H, C – H stretch	Alkynes terminal
3194.23	= C – H stretch	Aromatics
3009.05	= C – H stretch	Alkene
2931.90	C – H stretch	Alkane
2661.85	– H – C – O stretch	Aldehydes
2191.21	– C ≡ C – stretch	Alkyne
1743.71	–C = O stretch	Carboxylic acid
1450.52	C – H bond	Alkane
1365.65	– C – H bond	Alkane
1234.48	– C – N stretch	Aliphatic amine
1157.33	– C – H wag(CH_2X)	Alkylhalide

This confirms that most of the phytochemicals facilitated capping at different surfaces of the nanoparticles and also confirmed that there was an interaction between the formed AgNPs and the phytochemicals in the plants (Akpanudo and Olabemiwo, 2024b)

In Fig. 5, an SEM micrograph of AgNPs is shown and reveals a porous surface Fig. 5a shows that the particles in the micrograph appeared highly magnified. It also displayed irregularly shaped and textured particles. Also, the particles tend to exhibit intricate details at a microscopic level, revealing their unique surface features. However, the Sem micrograph (Fig. 4b) after adsorption shows spherical structures like pollen grains. The surface of the AgNPs appeared textured and uneven, which is due to the adsorbed Cr^{3+} ions. There was no prominent visibility concerning ridges, which was found in Fig. 4a, indicating that the adsorbate sufficiently covered them. The image was captured at a high magnification.

The examination of the composition of the nanoparticles through energy-dispersive X-ray technology indicated results that are contained in Table 3. The most abundant element in these silver nanoparticles is carbon, followed by oxygen and nitrogen Interestingly, the silver content is significant, accounting for 26.71% of the composition. These results provide valuable insights into the elemental makeup of the nanoparticles The carbon, nitrogen and oxygen originate from the plant extract and are additional capping agents that can also facilitate its adsorption properties.

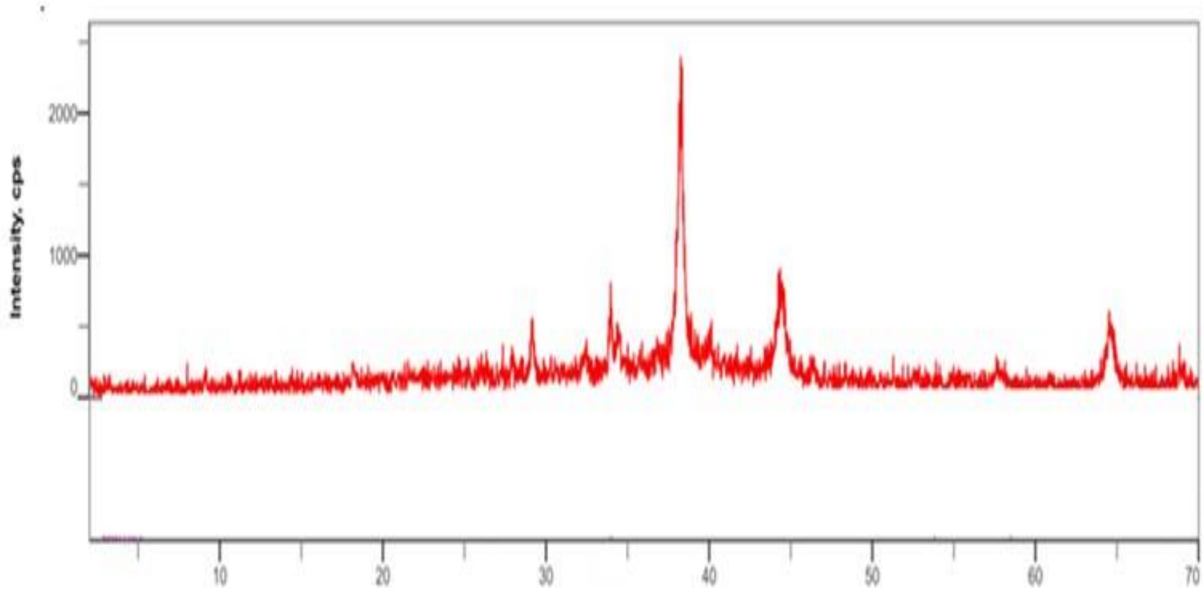

Fig.4: Silver nano-particles XRD Spectra

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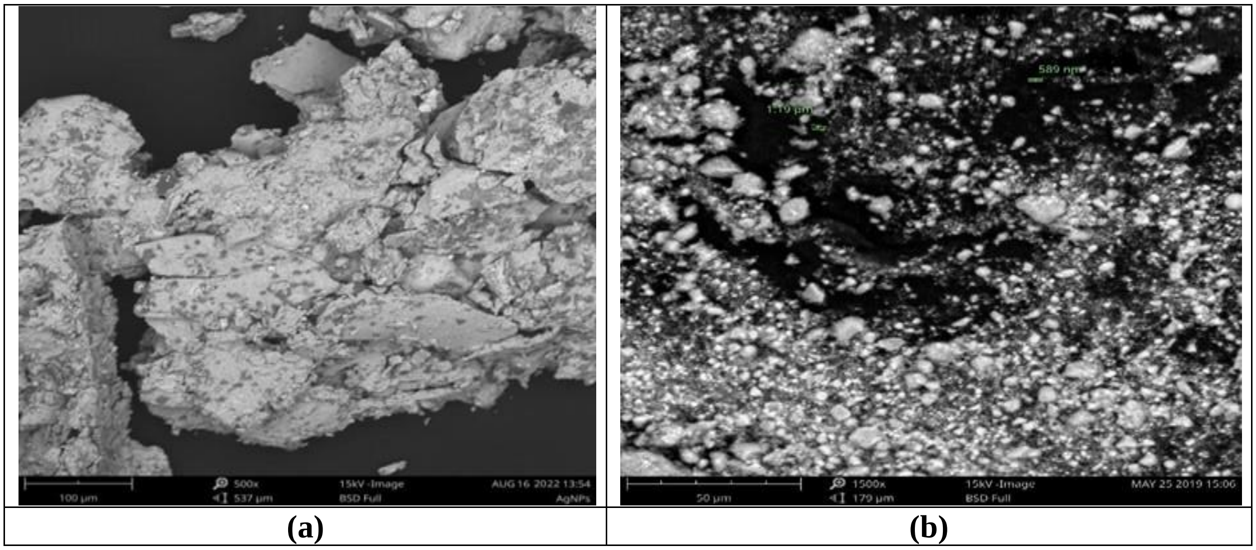

(a) **(b)**

Fig. 5: SEM micrographs of AgNPs (a) before adsorption (b) after adsorption of Cr^{3+}

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Table 3: Energy Disperse Spectroscopy (EDS) of silver

Element Number	**Element Symbol**	**Element Name**	**Atomic Conc.**	**Weight Conc.**
6	C	Carbon	60.33	55.33
8	O	Oxygen	32.93	33.15
7	N	Nitrogen	3.46	3.47
26	Fe	Iron	0.50	2.00
14	Si	Silicon	0.78	1.56
20	Ca	Calcium	0.37	1.07
13	Al	Aluminium	0.39	0.76
19	K	Potassium	0.24	0.66
11	Na	Sodium	0.35	0.57
17	Cl	Chlorine	0.17	0.44
16	S	Sulfur	0.16	0.36
12	Mg	Magnesium	0.18	0.32
15	P	Phosphorus	0.14	0.31
47	Ag	Silver	26.71	30.31

3.2 Adsorption study

Fig. 6 below shows plots indicating the variation of percentage removal of Cr3++ with (a) time (b) adsorbent dosage and (c) temperature. The three plots reveal that the percentage of chromium ions removed through adsorption at various times showed an increment translating to efficiency of % (at 10 minutes) to 63.31% after a contact time of 50 minutes The increase in adsorption with time is due to the progressive filling of the available and active adsorption sites with time until all the sites are filled. It is apparent from the plot (Fig. 5a) that the steepness of the plot started decreasing after 40 minutes of contact which confirmed why the adsorption rate started decreasing after this time. Although this study did not cover a wider range of contact time that would have presentd more information. It is most likely that the time for optimum absorption is 40 minutes.

A relatively linear plot was also observed concerning the variation of the aamount of Cr^{3+} removed from the contaminated solution. However a decrease in adsorption was observed between 0.2 and 0, 4 g dosage which may be due to the adjustment associated with equilibration process. Beyong this dosage (0.4 g), the adsorption capacity of the materials increases with an increase in dosage. This confirms that an increase in surface area of contact (which was achieved by an increase in dosage) led to an increase in adsorption from 94 to 98% within the investigated dosage range (Eddy *et al*., 2023; Garg *et al*., 2022). Similar observations have been reported by Akpanudo and & Olabemiwo (2024) for the adsorption of polyhydrocarbon by AgNPS.

The observed increase in the percentage Cr^{3+} removed from the solution with an increase in temperature signified that tha adsorption process favours chemisorption mechanism, whish is a mechanism that operate when adsorption is favoured with an increase in temperature (Odoemelam and Eddy, 2008).

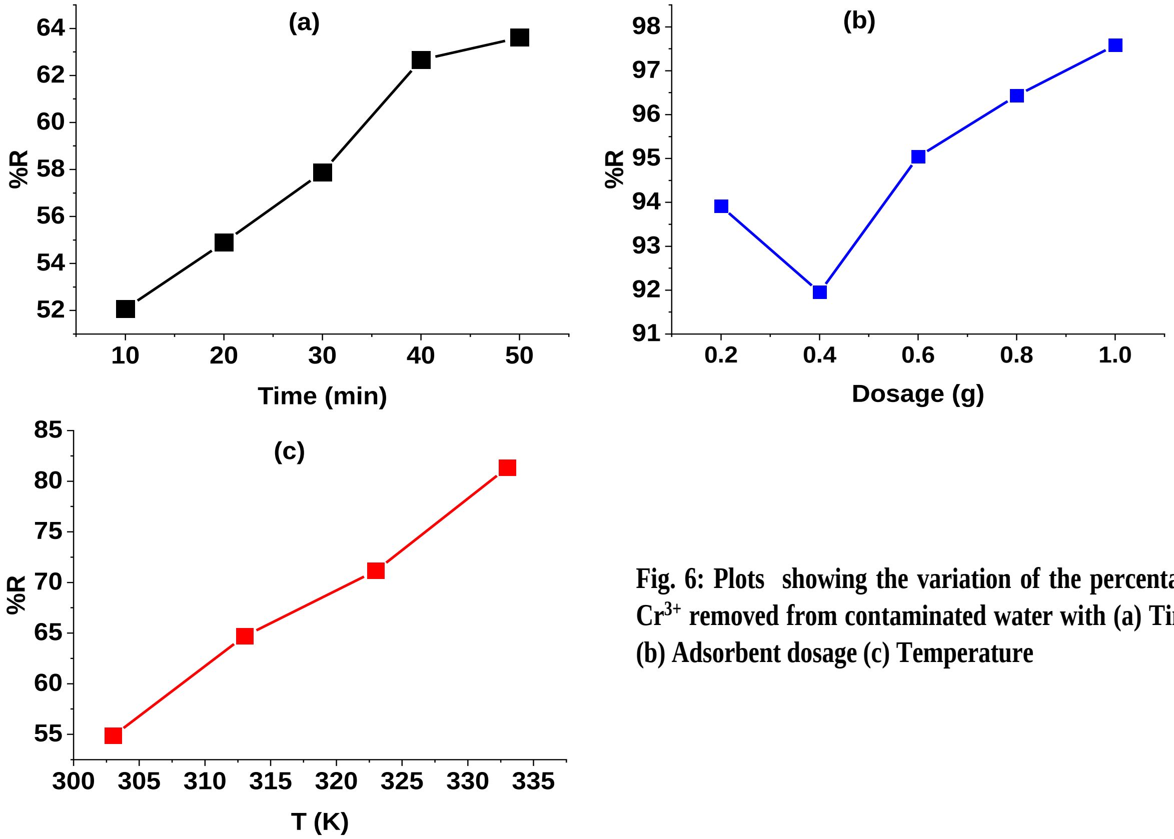

Fig. 6: Plots showing the variation of the percentage Cr^{3+} removed from contaminated water with (a) Time (b) Adsorbent dosage (c) Temperature

Generally, results obtained for the adsorption removal of chromium ions from aqueous solution by some nanoparticles , are in close agreement with some literature values, which are shown in Table 4.

Table 4: Some literature values for the adsorption efficiencies of various materials for the removal of Cr^{3+}

Nanoparticle	Chromium (Cr) Form Targeted	Removal Efficiency	Reference
Iron Oxide (Hematite)	Cr(VI)	82-90%	Liu, *et al.*. (2012).
Zero-valent Iron Nanoparticles (PU@nZVI)	Cr(VI)	99.98% (tap water), 96.81% (industrial effluent), 94.57% (treated sewage)	Li, *et* al. (2023).
Titanium Dioxide (TiO_2)	Cr (unspecified)	Efficiency varies depending on synthesis and conditions	Alsamer *et al.* (2022).
Mesoporous Silica Nanoparticles (NH_2-MSNs)	Cr(VI)	76.8%	Wei *et al.* (,2020).
Polyaniline (PANI)	Cr(VI)	Up to 180 mg/g	Fu *et al.* (2018).. DOI: 10.1016/j.cej.2018.05.092: [invalid URL removed]

4.0 Conclusion

The study successfully demonstrated the green synthesis of silver nanoparticles using leaf extracts from the Roster tree. The characterization of refinery wastewater and the determination of heavy metal content were crucial steps in understanding the environmental impact. The use of AgNPs synthesized through this eco-friendly method holds promise for various applications. In view of the observed findings and the need for improvement, recommendations for future research on the investigation of the physicochemical properties of the synthesized AgNPs, such as size, shape, and stability and the assesement of the potential toxicity and biocompatibility of the nanoparticles

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Compliance with Ethical Standards Declarations

The authors declare that they have no conflict of interest.

Data availability

All data used in this study will be readily available to the public.

Consent for publication

Not Applicable

Availability of data and materials

The publisher has the right to make the data Public.

Competing interests

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