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Article

Preparation, characterization of *Telfairia occidentalis* stem extract-silver nanocomposite and application in remediation of lead (ii) ions from oilfield produced water

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Abstract: Every production day in Nigeria, and in other oil producing countries, millions of barrels of produced water is generated. Being very toxic, remediation of the produced water before discharge into environment or re-use is very essential. An eco-friendly and cost effective approach is hereby reported for remediative pre-treatment of produced water (PW) obtained from Nigerian oilfield. In this approach, *Telfairia occidentalis* stem extract-silver nanoparticles (TOSE-AgNPs) were synthesized, characterized and applied as bio-based adsorbent for treating the PW *in situ*. The nanoparticles were of average size 42.8 nm ± 5.3 nm, spherical to round shaped and mainly composed of nitrogen and oxygen as major atoms on the surface. Owing to the effect of addition of TOSE-AgNPs, the initially high levels (mg/L) of Total Dissolved Solids (TDS), Biological Oxygen Demand (BOD) and TSS of 607, 3.78 and 48.4 in the PW were reduced to 381, 1.22 and 19.6, respectively, whereas DO and COD improved from 161 and 48.4 to 276 and 19.6 respectively, most of which fell within WHO and US-EPA safe limits. Particularly, the added TOSE-AgNPs efficiently removed Pb (II) ions from the PW at temperatures between 25 °C to 50 °C. Removal of TOSE-AgNPs occurred through the adsorption mechanism and was dependent contact time, temperature and dose of TOSE-AgNPs added. Optimal remediation was achieved with 0.5 g/L TOSE-AgNPs at 30 °C after 5 h contact time. Adsorption of Pb (II) ions on TOSE-AgNPs was spontaneous and physical in nature with remediation efficiency of over 82% of the Pb (II) ions in solution. Instead of discarding the stem of *Telfairia occidentalis,* it can be extracted and prepared into a new material and applied in the oilfield as reported here for the first time.

Keywords: adsorption; heavy metals removal; nanomaterial; oilfield chemical; remediation; water treatment

1. Introduction

During production of crude oil, water is usually also co-produced. This water is often referred to as produced water (PW) or petroleum wastewater. The PW may originate from reservoir or formation water, or water injected during recovery or enhanced recovery operations [1]. The chemical composition of PW varies depending on geographical region, quality of crude and operating condition [2]. Most often, PW is composed of a complex blend of both inorganic and organic compounds. This implies that PW is highly toxic, and when discharged into the environment, it pollutes the environment. Being a mixture of complex toxic organic and inorganic in nature, the chemicals in PW are often resistant to chemical or biological degradation. Discharge of PW on soils or into water has been a major cause of environmental degradation in the Niger delta region of Nigeria [3]. It renders water unfit for consumption, harms aquatic animals, kills biodiversity on the land and renders the soil infertile for cropping. In the end, it leads to decline in food production which may result to famine, malnutrition and even deaths.

To guard against these menace, it is very crucial that PW be treated before being discharged into the environment or re-use in injection stream. Otherwise, the discharge could be pose harmful (carcinogenic, mutagenic) effects on environment and humans [3] and cause corrosion, scaling and flow problems in transportation pipework [4]. Depending on its composition, various techniques have been applied to treat PW. Among these include physicochemical, chemical and biological methods of PW treatment described in literature [5,6]. Comparatively, chemical methods of treatment are very popular and reputed for good efficiency and selectivity [7–10]. For instance, high concentrations of grease, oil and fats as well as pollutants that may be suspended or dissolved in PW have been resolved by using chemical methods such as coagulation [11]. The coagulants precipitates are dissolved or suspended as colloidal solids which makes it easy to separate them by sedimentation. Electrocoagulation may also be efficient especially for resolving very greasy and oily PWs [12,13]. Experts have opined that a single method may not remove all the toxic components in PW at the same time. Therefore, any method used is often designed towards removing either some very toxic inorganic components only or some very toxic organic components only, at a given time [11].

This study was designed from this background and was aimed at removing some major toxic inorganic components in PW. The toxic inorganic substances in PW are basically heavy metals ions such as lead, cadmium, and chromium. These ions are often better removed using adsorbents by the adsorption [11]. Adsorption phenomenon is a popular method of treating PW [14]. For instance, activated carbon prepared from various sources is a commonly reported efficient adsorbent for petroleum wastewater treatment [15,16]. In selecting an adsorbent, cost effectiveness, local availability, renewability, durability, stability, biodegradability, eco-friendliness and high adsorption capacity are key factors often considered [14,17]. Despite the efficiency, activated carbon is very expensive to buy and laborious to fabricate and characterize. Scientists have therefore been in the search for cheap alternative materials, hence the proposed research work.

These days, engineered materials from plant extracts have been explored as alternative adsorbents that satisfy many of the requirements mentioned above [18]. Among the ones reported, plant-based adsorbents (biosorbents) have been demonstrated to be effective in removing some organic compounds and heavy metal ions from industrial wastewater [19–22]. Apart from a recent report by Ituen and co-workers [11], to the best of our knowledge, the use of plant biomass-based adsorbents in its nano-form to remove heavy metals from produced water has not been reported in literature, hence the motivation for this study. In this study, we have demonstrated the use of *T. occidentalis*-silver nanoparticles as adsorbent for treating PW for the first time.

Adsorbents derived from plant biomasses appear to be desirable because it will be of low cost, non-toxic and sustainably obtainable. Also, since plants contain a wide range of phyto-compounds, it could be multifunctional but, would easily be degraded by biochemical agents [11]. In other words, if stored for long, biochemical degradation of the biomass sets in, then its adsorption capacity and efficiency declines. To overcome these setbacks, the extract needs to be modified using chemical additives [23]. Recently, nanoparticles composites prepared by bio-reduction of plant extracts, have been used to remove toxic heavy metal ions, especially Pb, Cd, Cr and organic pollutants from wastewater [11]. Since nanoparticles large surface to volume ratio, their reactivity is expected to be high and this could justify the high removal efficiency reported in literature [11]. Also, being less difficult to synthesize, with the synthetic process not requiring deployment of expensive equipment or high energy, nanoparticles engineered from plant extracts would be more desirable. Therefore, the main objectives of this research was to prepare bio-based silver nanoparticles from *T. occidentalis* stem extract, characterize the nanoparticles and apply it as adsorbent for remediative treatment of PW, especially to remove Pb (II) ions from the PW.

2. Materials and methods

2.1. Sample collection and preparation

Viable seeds of *T. occidentalis* were obtained from Akwa Ibom Agricultural Development Program (AKADEP) and were authenticated by a plant taxonomist in the Department of Botany and Ecological Studies in the University of Uyo. The plants were cultivated in the field. Field experiment adopted a completely randomized design (CRD) with three replications. The plants were cultivated in three raised shaped beds and maintained under proper routine agronomic practices [24]. The mature plant was harvested and the edible leaves plucked out. The stem (which is often discarded) were cut into pieces, washed convincingly with distilled water, dried in air at laboratory temperature and macerated (**Figure 1a–c**).

(a) de-leaving. **(b)** cutting into small sizes. **(c)** maceration.

Figure 1. *T. occidentalis* stem after **(a)** de-leaving; **(b)** cutting into small sizes; **(c)** maceration.

2.2. Preparation of T. occidentalis stem extract

A 10 g of the macerated sample was soaked in 1 L of de-ionized water for 24 h and filtered using 1 mm filter paper. The filtrate was concentrated to paste form in rotary evaporator at 40 °C, dried in oven at 40 °C and blended in mortar to obtain dry powdery *T. Occidentalis* stem extract (TOSE).

2.3. Preparation of TOSE-silver nanomaterial

Solution of 0.001 M $AgNO_3$ (Analar, BDH, England) and 1.0 g/L of TOSE were prepared in deionized water. Both were mixed at various ratios (vol/vol), allowed to react and observed for colour change [11]. Every 1 hour, aliquot of the mixture was subjected to UV-Vis spectroscopic analysis. After colour change, a portion of the mixture was concentrated in rotary evaporator at 40 °C, then retrieved, washed using de-ionized water and filtered. The filtrate was dried in oven at 30 °C and labelled as TOSE-Silver nanomaterial (TOSE-AgNP) and stored in aluminum foil for characterization. Another portion was stored in amber colored glass for future analyses.

2.4. Characterization of synthesized materials

UV-Vis analysis was conducted by scanning both the TOSE and TOSE-AgNPs at 200–800 nm using Thermo Genesys 10 UV/Vis spectrophotometer. The functionalities in small quantity of each of TOSE and TOSE-AgNP (mixed with KBr) were determined by FTIR using Agilent cary 630 FTIR/ATR spectrophotometer. The crystallographic properties of the powder samples of both TOSE and TOSE-AgNP were also analyzed by XRD at $2\theta = 10°–90°$ using PX1800 X-ray diffractometer. The elemental compositions of each of TOSE and TOSE-AgNP were determined by EDS using Phenom ProX SEM/EDS spectrophotometer. The morphology and size of each of TOSE and TOSE-AgNPs were probed by TEM using Fei Technai G2F20 microscope.

2.5. Collection and treatment of produced water

Produced water was collected from Total Oil drilling platform at Amenem near Port Harcourt and transported to the laboratory the same day. The water sample was analysed to determine the average concentrations of lead ions present following standard procedures already reported by Ituen and co-workers [11]. In addition, some physicochemical properties of the water, namely, biochemical oxygen demand (BOD_5), total dissolved solids (TDS), chemical oxygen demand (COD), conductivity, total suspended solids (TSS), dissolved oxygen (DO) and pH were also analysed following similar procedures reported by Ituen and co-workers [11].

2.6. Remediation of heavy metals from produced water

The procedures reported by Ituen and coworkers [11] were also followed with slight modifications. About 50 mL each of the produced water were placed in several flasks. About 0.5 g/L of TOSE and 0.1 g/L to 0.5 g/L of TOSE-AgNPs was added to each flask and each mixture was shaken in water bath at room temperature for 5 h. After 5 h, each mixture was filtered, and each filtrate was analyzed by AAS to determine the concentrations of each of Pb (II) ions.

2.7. Effect of adsorbent concentration

The TOSE-AgNPs was prepared into five (5) different concentrations to elucidate the effect of its dosage on the remediation efficiency. The concentrations were selected between 0.10 g/L to 0.50 g/L and this was obtained by dilution of the highest concentration using the dilution principle. During this investigation, the contact time, temperature and volume of the PW were not changed.

2.8. Effect of time and temperature

To determine the effect of time on the remediation efficiency, aliquots of the mixture at room temperature were collected every 1 hour within the shaking process and analysed by AAS. Also, the influence of temperature on the remediation efficiency was studied by varying the temperature of the solution in the water bath between 25 °C to 50 °C. For this experiment, the highest concentration of TOSE-AgNPs (0.50 g/L) was used and the shaking process was carried out at a constant time of 5 h.

2.9. Analysis of data

The concentration of each metal ion in the produced water before remediation was denoted by C_o while the equilibrium concentration of each metal ion after filtration was denoted by C_e. The remediation efficiency (η) was determined in terms of the ratio of the amount of heavy metal adsorbed by the substrate using Equation (1) [11].

$$\eta(\%) = \frac{C_o - C_e}{C_o}\ x\ 100 \tag{1}$$

The amount of heavy metal ion adsorbed per unit mass of TOSE and TOSE-AgNPs at equilibrium (q_e) was determined from Equation (2), where M represents the mass of the adsorbent added to heavy metal ions solution of and V is the volume of the solution.

$$q_e = (C_o - C_e)\frac{V}{M} \tag{2}$$

3. Results and discussion

3.1. Formation of nanoparticles

On observation after every 1 h, the colour of the mixtures changed gradually until the nanoparticles were fully developed, signified by a change in colour from dark green to brown. It took different duration for complete development of the nanoparticles to occur depending on the ratio of mix. For instance, for the mixture containing TOSE:$AgNO_3$ (vol/vol) at 1:1 formed at about 2 h whereas 1:2 and 2:1 formed at about 5 h and 8 h respectively. Only the nanoparticles formed from 1:1 at the shortest duration was used for further studies.

3.2. Characterization of nanoparticles

3.2.1. UV-Vis spectroscopy

Both TOSE and TOSE-AgNPs were subjected to UV-Vis analyses and the spectra obtained were shown in **Figure 2**. It can be observed that TOSE produced absorption maximum corresponding to the maximum wavelength of absorption (λ_{max}) at 433 nm whereas that of TOSE-AgNPs was obtained at 485 nm. Since the absorption (λ_{max}) for TOSE and TOSE-AgNPs were different, it was inferred that TOSE-AgNPs is a different material from TOSE. Also, the (λ_{max}) obtained for TOSE-AgNPs were compared to others reported in literature for silver nanoparticles [11]. It was observed that the value for TOSE-AgNPs falls within 450–520 nm which is the range often obtained for silver nanoparticles. Therefore, the (λ_{max}) obtained in the present study agrees with those reported in literature [11,18].

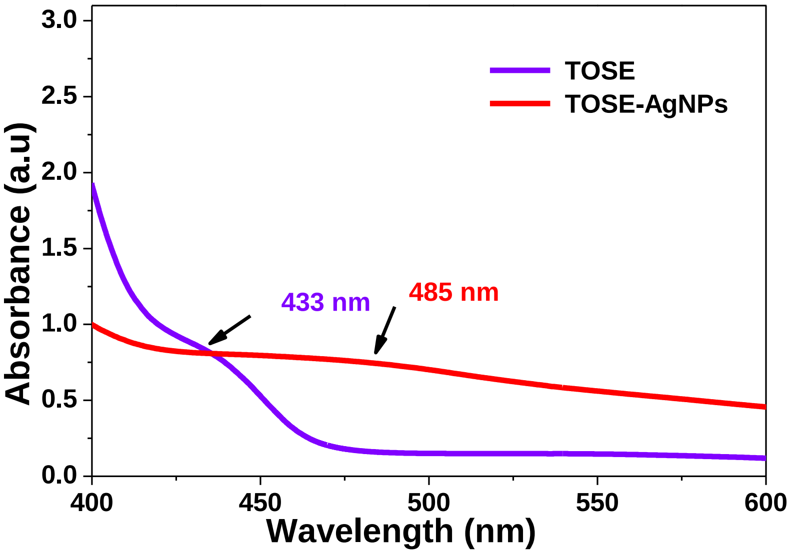

Figure 2. UV-Vis spectra of TOSE and TOSE-AgNPs.

3.2.2. FTIR spectroscopy

In order to elucidate the functional groups present in each of the material, the FTIR spectra of TOSE and TOSE-AgNPs were obtained and plotted in one frame of axes for easy comparison. The spectra obtained were shown in **Figure 3**. It can be observed from the figures that TOSE produced several peaks including in the fingerprint region. However, the peaks at around 3120–3530 cm^{-1}, 2975 cm^{-1} and 1620 cm^{-1} were of significance to this study. The 3120–3530 cm^{-1} peak on TOSE spectra may be assigned to O-H stretching of an aromatic alcohol or N-H stretching of a primary amine group. On formation of TOSE-AgNPs, it can be observed that this peak became broader and more prominent than with the crude extract. A similar occurrence was observed with the peak at 2975 cm^{-1} which may be assigned to N-H stretching of an amine salt. This peak appears sharper and more prominent with TOSE-AgNPs than TOSE, suggesting that an amine salt may have been formed with silver. The peak at 1620 cm^{-1} may be assigned to C = C of alkene or α, β-unsaturated ketone. This peak shifted to 1635cm^{-1} in the spectrum of TOSE-AgNPs and became more prominent. This indicates possibility of interaction of silver ions with TOSE phyto-compounds at the C = C sites to form TOSE-AgNPs.

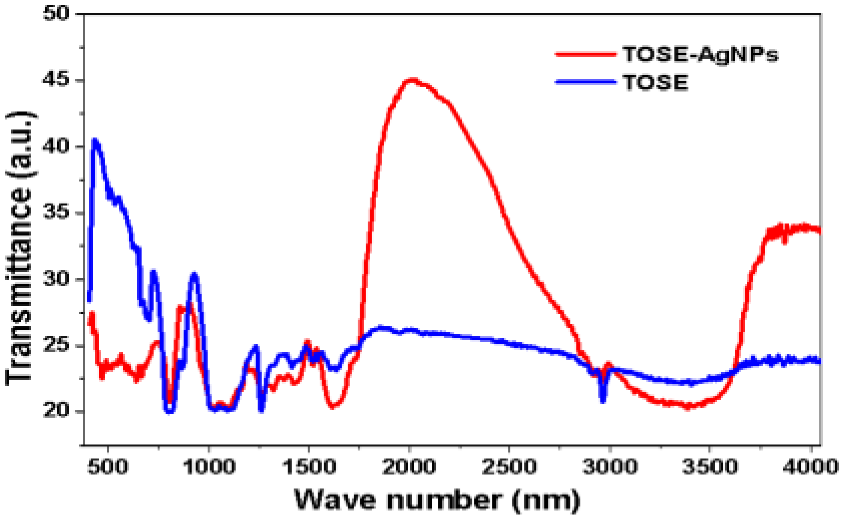

Figure 3. FTIR spectra of TOSE and TOSE-AgNPs.

3.2.3. XRD spectroscopy

To determine whether TOSE-AgNPs were crystalline, they were subjected to XRD analyses alongside with TOSE for proper comparison and the spectra obtained were shown in **Figure 4**. It was observed that the spectrum of TOSE yielded no peaks whereas that of TOSE-AgNPs yielded major peaks at 2θ = 28.0°, 32.5°, 38.2°, 44.0°, 46.4°, 64.3° and 77.6°.These peaks were compared to silver file 04–0283 of Joint Committee on Powder Diffraction Standards (JCPDS) card as well as with other reports on plant extracts mediated silver nanoparticles [11]. It was observed that the peaks at 32.5°, 38.2° and 44.0° correspond to (121), (111) and (200) planes of Ag^0 phase. The peak at 38.2° was the most prominent, indicating that the silver is mostly distributed in the Ag (111) plane. Comparing the spectrum of TOSE with that of TOSE-AgNPs, it was clearly observed that while TOSE was amorphous, TOSE-AgNPs were crystalline, indicating that TOSE-AgNPs may be a nanoparticle.

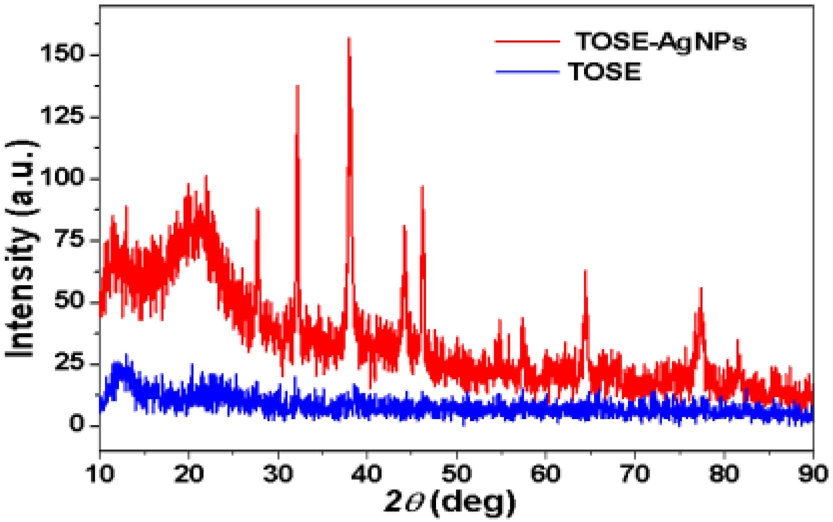

Figure 4. XRD diffraction patterns of TOSE and TOSE-AgNPs.

3.2.4. EDS spectroscopy

The EDS spectra of TOSE and TOSE-AgNPs with prejudice to C, N, O and Ag atoms were obtained for comparison as shown in **Figure 5**. The result revealed that Ag was present on the surface of the new material (TOSE-AgNPs) but not found on TOSE. Though both contain C, N and O, the amounts were different as shown in **Table 1**. It can be inferred from **Table 1** that the incorporation of silver into the phyto-compounds of TOSE resulted in its binding and formation of a kind of Ag-organic framework which increased the visibility of N and O. A similar suggestion was made in a work reported by Ituen and coworkers [11]. The EDS results obtained also supported that TOSE-AgNPs may have been formed and may be nanocomposite.

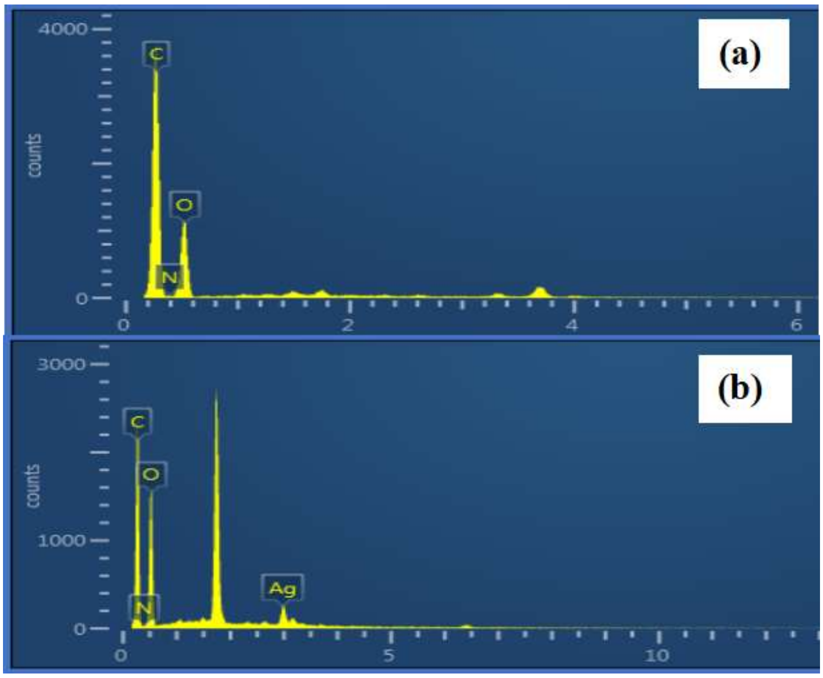

Figure 5. EDS spectra of (**a**) TOSE and (**b**) TOSE-AgNPs.

Table 1. Elemental composition of TOSE and TOSE-AgNPs surface determined by EDS.

Element	**TOSE**		**TOSE-AgNPs**	
	Weight (%)	**Atomic (%)**	**Weight (%)**	**Atomic (%)**
C	70.02	75.03	46.12	58.16
N	0.46	1.01	1.13	2.21
O	29.52	23.96	39.34	37.73
Ag			13.41	1.91

3.2.5. Transmission electron microscopy

The nanostructure of TOSE-AgNPs was probed using transmission electron microscopy and the images captured for both TOSE and TOSE-AgNPs were shown in **Figure 6**. It was observed that TOSE were shapeless and sized within the micro-scale whereas TOSE-AgNPs were spherical to round and of average sizes of 42.8 nm

± 5.3 nm. TEM results confirmed that TOSE-AgNPs was nanomaterial and appeared crystalline.

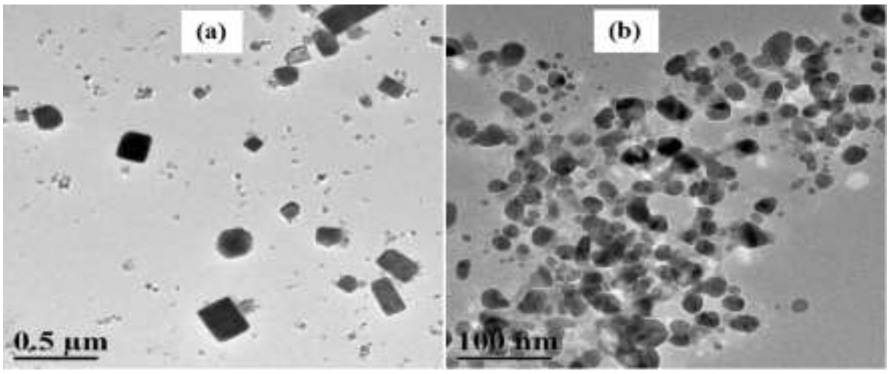

Figure 6. Morphologies of (**a**) TOSE and (**b**) TOSE-AgNPs determined by TEM.

3.3. Physicochemical properties of produced water

The concentration of Pb (II) ions in the produced water (PW) was determined in triplicates and the average values as computed was 1.43 ± 0.08 mg/L. The other physicochemical properties determined are shown in **Table 2**. It has been documented that the USA-EPA and WHO permissible limits of Pb (II) ions for drinking water is 0.015 mg/L and 0.010 mg/L respectively [11], indicating that Pb (II) ions are present in excess amount and remediation is crucial. In addition, the values obtained for key pollution indicator parameters such as TSS, TDS, BOD etc were above WHO standards, therefore would require remediation to reduce them to safe limits before discharge or re-use for injection. Therefore, the PW was initially remediated by addition of TOSE and TOSE-AgNPs and the results from both adsorbents were compared and discussed in the following sub-sections.

Table 2. Physicochemical properties of non-remediated and remediated produced water.

Parameter	Non-remediated water sample	Remediated with TOSE	Remediated with TOSE-AgNPs
pH	8.55	8.52	8.56
Conductivity (µScm^{-1})	4318	3953	2881
TDS (mg/L)	607	406	381
BOD$_5$ (mg/L)	3.78	1.56	1.22
DO (mg/L)	2.16	5.87	6.79
COD (mg/L)	161	242	276
TSS (mg/L)	48.4	38.2	19.6

3.3.1. Effects of addition of TOSE and TOSE-AgNPs

From **Table 2**, it can be observed that remediation of PW with TOSE reduced pH from 8.55 to 8.52 whereas using TOSE-AgNPs, the pH rather increased to 8.56. These levels were well within the permissible limits by both US-EPA and WHO. For conductivity, it can be observed that PW had a very high value of 4318 µScm^{-1}. However, on remediation with TOSE and TOSE-AgNPs, the values reduced to 3953 µScm^{-1} and 2881 µScm^{-1} respectively. This implies that remediation with TOSE and TOSE-AgNPs caused significant reduction in conductivity of PW. Although the final conductivity of remediated water was still higher than the permissible level for drinking water (2500 µScm^{-1}) and may require further treatment, the resulting water could still be useful for irrigation purposes and for livestock, which requires conductivity of around 2000–2500 µScm^{-1} ** [11]. For TDS, addition of TOSE and TOSE-AgNPs reduced the value from 607 mg/L to 406 mg/L and 381 mg/L respectively. The upper safe limit of TDS in drinking water was 500 mg/L while the WHO recommended limit is 300 mg/L. This implies that the TDS in PW made it unsafe for drinking but on remediation, safe limits were attained. Similarly, the safe limits for BOD, DO, COD and TSS are 1–2 mg/L, 6.5–8 mg/L, 250–500 mg/L, 30 mg/L respectively. For DO and COD, the values are associated with the amounts of oxygen in the water. The untreated water had low amounts of oxygen. However, on treatment with the new material, the amount of oxygen increased, which indicates its higher propensity to support aquatic life. As can be observed from **Table 2**, on remediation with TOSE and TOSE-AgNPs, significant improvements were obtained, and the physicochemical properties of the remediated water was within ranges of values close to safe or permissible levels. Thus, TOSE and TOSE-AgNPs were effective in remediating the PW with TOSE-AgNPs which showed better remediating effect than TOSE.

3.3.2. Effects of changing the concentration of TOSE-AgNPs

The concentration of TOSE-AgNPs was varied between 0.1 g/L to 0.5 g/L to elucidate the effect of its dose on the efficiency of remediation of Pb (II) ions. Results obtained are displayed in **Table 3**. It was observed that the concentration of Pb (II) ions in PW reduced from 1.43 mg/L to 0.32 mg/L and 0.18 mg/L on addition of TOSE and TOSE-AgNPs respectively, corresponding to an efficiency of 77.5% and 87.6% respectively. This implies that the efficiency of remediation of Pb increases with increase in TOSE-AgNPs dosage or concentration and is also in agreement with previous observations reported by Ituen and coworkers [11]. A possible explanation for this trend is that as the dose of the adsorbent increases, more adsorption sites becomes available per volume of the PW due to the presence of more adsorbent species in solution. The more the adsorption sites, the more the number of Pb (II) ions adsorbed and sequestrated from the PW. On the other hand, even lower concentrations of TOSE-AgNPs were more efficient than 0.5 g/L TOSE supporting that TOSE-AgNPs performs better than the crude extract.

Table 3. Results for adsorption of lead (II) ions from PW within 5 h at room temperature using TOSE and different concentrations of TOSE-AgNPs.

Adsorbent	C_o **(mg/L)**	C_e **(mg/L)**	η **(%)**	q_e
0.5 g/L TOSE	1.43	0.41	71.2	102
0.1 g/L TOSE-AgNPs	1.43	0.32	77.5	555
0.2 g/L TOSE-AgNPs	1.43	0.28	80.4	288
0.3 g/L TOSE-AgNPs	1.43	0.26	81.8	195
0.4 g/L TOSE-AgNPs	1.43	0.20	86.1	154
0.5 g/L TOSE-AgNPs	1.43	0.18	87.6	125

3.3.3. Effects of temperature

The effect of temperature on the amount of Pb (II) ions removed from the PW was investigated by varying the experimental conditions from room temperature (25 °C) to 50 °C and the results obtained are shown in **Table 4**. The results reveal that as temperature increases, the amount of Pb (II) ions removed as well as the remediation efficiency decreases. For instance, in the presence of TOSE, the amount of Pb (II) ions in PW reduced from 1.43 mg/L to 0.42 mg/L and 0.58 mg/L respectively corresponding to remediation efficiency of 70.7% and 59.7% respectively as temperature increased from 25 °C to 50 °C. This indicates that as temperature increases, there would be a huge reduction in remediation capacity and the q_e when TOSE is used as adsorbent. However, on addition of TOSE-AgNPs, the reduction in remediation efficiency was only slightly as could be observed going from 85.2% to 81.6%. This implies that the modification of TOSE into TOSE-AgNPs makes it more thermally stable and efficient than TOSE. The observed decrease in remediation efficiency as temperature increases is could be ascribed to the weak binding character of the adsorbent—Pb (II) ions adsorptive interaction. Such interactions are usually considered as physisorptions and are often driven by physical forces such as electrostatic interaction between positive Pb (II) ions and negative groups on the TOSE-AgNPs surface [11]. Owing to their weak nature, such interactions weaken with increase in temperature, leading to reduced remediation efficiency.

Table 4. Results for adsorption of lead (II) ions from produced water within 5 h at different temperatures.

Temperature (°C)	**TOSE**			**TOSE-AgNPs**		
	C_o (mg/L)	**C_e (mg/L)**	**η (%)**	**C_o (mg/L)**	**C_e (mg/L)**	**η (%)**
25	1.43	0.42	70.7	1.43	0.21	85.2
30	1.43	0.41	71.4	1.43	0.17	88.1
40	1.43	0.48	66.4	1.43	0.22	84.3
50	1.43	0.58	59.7	1.43	0.26	81.6

3.3.4. Effects of contact time

The effect of contact time between the adsorbent and the heavy metal contaminants in PW was investigated to elucidate the optimum time required to remove the ions from PW. The results obtained were shown in **Table 5**. From the table, it can be observed that the efficiency of remediation increased as contact time increased until it reached a critical time of 5 h after which there was no significant increase in the percentage remediation efficiency. Therefore, it was inferred that the time taken for TOSE-AgNPs to optimally remove Pb ions from PW is 5 h. After this time, equilibrium may have been achieved and an optimal efficiency reached.

Table 5. Results for adsorption of lead (II) ions from produced water at room temperature and different times using 0.50 g/L TOSE-AgNPs.

Time (h)	**Parameters**		
	C_o **(mg/L)**	C_e **(mg/L)**	η **(%)**
1	1.43	0.74	48.1
2	1.43	0.61	54.7
3	1.43	0.47	66.8
4	1.43	0.37	74.2
5	1.43	0.26	81.6
6	1.43	0.25	82.1
7	1.43	0.25	82.2
8	1.43	0.25	82.2

3.4. Remediation kinetics and adsorption mechanism

It has been reported that removal of heavy metal ions from solution by bio-based adsorbents occurs through the adsorption mechanism. Adsorption involves attraction and holding of the metal ions on the surface of the adsorbent molecules driven by surface forces. These surface forces could be electrostatic or weak van der Waals forces (physical adsorption) or even coordinate covalent bonding (chemical adsorption). To probe the nature of these forces, the values of q_e and C_e obtained were fitted into various adsorption isotherms but the best fit was obtained with the Freundlich adsorption isotherm (with $R^2 = 0.9998$) which can be represented as shown in Equation (3) [11]:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{3}$$

where K_f and n are constants related to the adsorption phenomena and K_f can be related to the free energy of adsorption using the Equation (4) [11]:

$$\Delta G_{ads} = -RT \ln 55.5 K_f \tag{4}$$

where 55.5 is a factor that relates with the concentration of water molecules. The obtained isotherms is shown in **Figure 7** and the associated kinetic parameters deduced. The straight line graph afforded a slope of 0.93 and an intercept of 1.814. The constants n and K_f were 0.551 and 1.08 respectively. The value of ΔG_{ads} obtained was −10.14 kJ/mol which can be appropriately associated with spontaneous adsorption of the metal ions on TOSE-AgNPs. Thus, if deployed for industrial use, TOSE-AgNPs would remediate PW on its own without the need for any catalyst or external force. Also, since the ΔG_{ads} value is less negative than −20 kJmol^{-1}, the adsorption therefore proceeded via the physical adsorption mechanism [11].

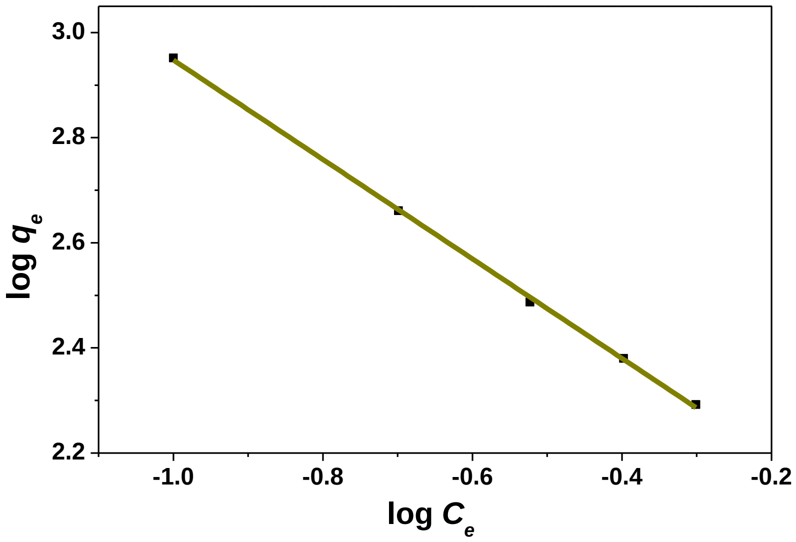

Figure 7. Freundlich adsorption isotherm for the adsorption of Pb from PW using TOSE-AgNPs at room temperature.

4. Conclusion

Telfairia occidentalis stem extract-silver nanocomposites (TOSE-AgNPs) were prepared, characterized and assessed as adsorbent for removing treatment of PW, which is usually toxic, before discharge or re-use. The nanomaterial was round shaped and the surfaces were rich in O and N atoms. The TOSE-AgNPs was up to 82% efficient in remediating Pb (II) ions from PW. Treatment of PW with TOSE-AgNPs also helped to reduce the levels (mg/L) of TDS, BOD and TSS while increasing the levels of DO and COD to near WHO and US-EPA safe limits. The remediation occurs through spontaneous physical adsorptive interactions between TOSE-AgNPs species and Pb (II) ions. The adsorption and remediation depends on contact time, temperature and dose of TOSE-AgNPs added. The new material could find application in the petroleum industry for treating associated wastewater.

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