Activated Carbons from *Gambeya Albida* and *Telfairia Occidentalis* Seed Shells: Effect of Activating Agent on the Removal of Pb(II) Ions from Aqueous Solutions

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Abstract: Activated carbons were produced from *Gambeya albida* and *Telfairia occidentalis* seed shells by chemical activation and their properties were determined. The effects of different production conditions (activating agent, carbonization temperature and carbonization time) were studied and it was found that activation with H_3PO_4 gave carbons with better properties than activation with NH_4Cl. Also, bulk density and % yield of the adsorbents decreased while surface area, total pore volume, % weight loss and % ash content increased with increase in carbonization temperature from 300 to 600 ^{o}C and carbonization time from 60 to 180 minutes for both raw materials. The potential of removal of Pb(II) ions from aqueous solution by selected activated carbon from both raw materials was also studied and it was found that the adsorption capacity was influenced by the contact time, initial Pb(II) concentration, solution pH, activated carbon particle size and dose as well adsorption temperature.

Introduction

Activated carbons (AC) are carbonaceous materials characterized by their extraordinarily large specific surface areas, well-developed porosity and tunable surface-containing functional groups[1]. Hence they are widely used as adsorbents for the removal of organic chemicals and metal ions of environmental or economic concern from air, potable water and wastewater[2].

Activated carbon can be produced from virtually any carbonaceous solid precursor by chemical or physical activation methods[3]. There is understandably a great effort to find low cost material to produce the AC[4]. A wide range of such precursors which have been studied include soybean oil cake[4], coal and coconut-based activated carbon[5], *Penthaclethra mycrophylla* woody pods[6], apricot stones[7,8], *Irvingia gabonensis* seed shell[9] and *Mangostana garcinia* shell[10]. Others include olive stone[11], lignin/wood[12], and spent coffee grounds and pomelo skin[13]. A number of reports exist on the removal of Pb(II) ions from water and wastewater[4,10-11,14-24].

Fluted pumpkin, Cucurbitaceae, is a green plant which widely grows in the West, East and Southern parts of Africa is produced in large quantities in these areas[25]. The chemical activating agents used in single-step method[26] in AC production include phosphoric acid, ammonium chloride, potassium hydroxide and zinc chloride. In this study, chemical activation was employed in producing activated carbon from two low-cost materials (*Gambeya albida* and *Telfairia occidentalis* seed shells). The objectives of this study were to ascertain whether the seed shells are suitable raw materials for the production of AC and to also determine the quality of the carbons produced as well as their effectiveness in the removal of lead from aqueous solutions.

Experimental

Telfairia occidentalis seed shell (TOSS) and Gambeya albida seed shell (GASS) were obtained from Nsukka environment, cleaned, dried, ground and then sieved to various particle sizes using EFL 2000/2 Sieve Shaker (CSC Scientific Company, Inc VA, USA).

Effect of activating conditions

Sieved materials with size 0.5 mm - 1 mm were used for this test. They were impregnated with 60% by weight H_3PO_4 and 60% by weight NH_4Cl solutions in 1:1 weight ratio for 24 h, after which they were drained and dried in an oven at 80 °C. They were then carbonized in a muffle furnace set at 300 °C. TOSS was left for 60 minutes while GASS was left for 90 minutes since it is harder. The resulting carbons were washed with distilled water until the pH of the leachate was up to 6 and then dried in an oven at 105 °C for 4 hours. For GASS, the raw GASS was used as the control while for TOSS, a third sample was carbonized without prior activation and was used as the control.

Effect of carbonization temperature and time

Study on the effect of carbonization temperature was conducted with raw materials that were retained in 0.5-1 mm sieve, activated with H_3PO_4 and then carbonized (60 min. for TOSS and 90 min. for GASS) at 300 °C, 400 °C, 500 °C and 600 °C. Raw materials with particle size 1-1.75 mm were used to study the effect of time on the AC activated with H_3PO_4 and carbonized (at 500 °C for TOSS and 600 °C for GASS) for 60, 90, 120, 150 and 180 min.

Characterization of adsorbents

Determination of yield and weight loss

The %yield and weight loss of AC were calculated using Eqs. 1 and 2.

$$\%Yield = \text{weight of AC/weight of precursor} \times 100 \qquad (1)$$
$$\%Weight\ loss = C\text{-}D/C\text{-}B \times 100 \qquad (2)$$

Where B is the mass of crucible and cover (g), C is the mass of crucible, cover and raw material, (g) and D is the mass of crucible, cover and activated carbon product (g).

Surface area measurement

The surface area of each adsorbent was determined according to the method of Al-Qodah and Shawarbkah[27]. In a typical experiment, 1.5 g of activated carbon was agitated in 100mℓ of HCl that had been diluted to pH of 3.0. Exactly 30 g of NaCl was added while stirring the suspension and the volume was made up to 150 mℓ with de-ionized water resulting in the change of the pH to 4.0. The pH was raised from 4 to 9 using 0.10N NaOH and the surface area calculated as follows:

$$S = 32V - 25 \tag{3}$$

Where S is the surface area (m^2/g) and V is the volume (mℓ) of 0.10N NaOH required to raise the pH from 4 to 9.

Determination of % ash content

The ash content of each adsorbent was determined according to ASTM D 2866[28] and the % ash content calculated from the combustion residue as follows using Eq. 4.

$$\text{\% Ash content} = W_{ash}/W_{ads} \text{ x } 100 \tag{4}$$

Where W_{ash} is the weight of dry ash (g) and W_{ads} is the weight of dry adsorbent (g).

This test was repeated until constant ash content was obtained.

Determination of bulk density and total pore volume

The apparent or bulk density of each adsorbent was determined by the tapping procedure[29]. The bulk density was then calculated using Eq. 5.

$$\text{Bulk density (g/mℓ)} = W_{mat}/V_{mat} \tag{5}$$

Where W_{mat} is the weight of dry material (g) and V_{mat} is the volume of dry material (mℓ).

The total pore volume of each adsorbent was determined according to the method of Gentscheva *et al.*[30].

Adsorption tests

The produced adsorbents were tested for their ability to remove Pb(II) ions in a batch adsorption process, in which 0.5 g of adsorbent was agitated with 100ml of 200 mg/ℓ Pb(II) solution for 4 hours. The adsorbents were removed by filtration and the residual metal concentration determined by atomic absorption spectrometry. Adsorption capacity of the adsorbents was calculated using equation (6)[11].

$$q_e = [(C_o - C_e) \text{ x } V] / m \tag{6}$$

Where q_e is adsorption capacity (mg/g), C_o and C_e are initial and equilibrium concentration, respectively (mg/ℓ), m is the adsorbent dosage (g) and V is the volume of solution (ℓ).

The effect of adsorption process variables was determined using TOSS (500 °C, 60 min.) and GASS (600 °C, 120 min.). The adsorption processes were carried out using various Pb(II) ion concentrations, solution pH, adsorbent particle sizes, adsorbent weights and adsorption temperature.

Results and Discussion

Characterization of adsorbents produced using different activating agents

The effects of different activating agents on the properties of the ACs are shown in Table 1. It can be seen from Table 1 that activation of the raw GASS resulted in increased surface area (SA), total pore volume (PV) and ash content as well as decreased bulk density.

Table 1. Effect of Activating Agent on Properties of GASS and TOSS

Parameter	H_3PO_4 Activation		NH_4Cl Activation	
	TOSS	GASS	TOSS	GASS
Yield, %	70.68	50.23	77.92	67.00
Weight loss, %	29.32	49.77	22.08	33.00
Surface area, m^2/g	612	791	516	692
Total pore volume, cm^3/g	2.17	2.27	1.82	1.77
Bulk density, g/cm^3	0.492	0.370	0.556	0.437
Ash content, %	1.50	1.70	0.60	0.89

The increase in PV and SA could both be as a result of the destruction of the aliphatic and aromatic species present in the raw materials by the activating agents leading to swift removal of volatile matters during the activation process[31]. This is due to higher burn-off of volatile matters (accompanied by the creation of meso- and macropores to the detriment of micropores[32] from the raw materials during carbonization with activating agents. The reduction of the volatile matter in the ACs creates a high percentage of calculated ash, since the ash is non-volatile. The increased SA implies higher adsorption sites for molecules to attach onto the surface of the carbon.

The changes in the measured parameters were found to be higher on AC prepared with H_3PO_4 with accompanying lower yield relative to AC activated with NH_4Cl. The foregoing suggests that activation with H_3PO_4 probably involved stronger reactions, such as oxidation of the raw materials, thereby leading to higher changes in the measured parameters. In fact, it has been noted that when heating the impregnated product in the carbonization stage, H_3PO_4 with the rise of temperature could be converted into phosphorus-containing constituents such as polyphosphoric acids ($H_n+2P_nO_{3n}+1$) that accelerate the carbonization of volatile components, resulting in increased porosity of the lignocellulosic material[32-34]. Activation followed by carbonization, however, resulted in higher weight loss and ash content as well as lower yield and bulk density.

Characterization of adsorbents carbonized at different temperatures

Table 2 shows the effect of carbonization temperature on the properties of the adsorbents produced using H_3PO_4 as activating agent. From the table, it is clear that the bulk density and yield of the adsorbents decreased while surface area, total pore volume, weight loss and ash content increased with increase in carbonization temperature from 300 °C to 600 °C for both raw materials. This trend could be attributed to the increase in thermal decomposition of the raw materials as the carbonization temperature increases[35], resulting in increased removal of volatile materials.

Table 2. Effect of carbonization temperature on properties of adsorbents produced using H_3PO_4 as activating agent

Parameter	300 °C		400 °C		500 °C		600 °C	
	TOSS	GASS	TOSS	GASS	TOSS	GASS	TOSS	GASS
Yield, %	50.23	70.68	46.90	67.12	42.77	62.64	38.84	58.12
Weight loss, %	49.77	29.32	53.10	32.88	57.23	37.36	61.16	41.88
Surface area, m^2/g	785	712	830	763	953	868	999	900
Total pore volume,cm^3/g	2.27	2.17	2.50	2.37	2.93	2.48	3.38	2.52
Bulk density, g/cm^3	0.370	0.492	0.357	0.485	0.324	0.468	0.290	0.452
Ash content, %	1.70	1.50	3.85	1.95	5.30	2.25	6.20	2.45

Since yield decreases with increase in carbonization temperature, production losses should therefore be considered in choosing the carbonization temperature for the production of AC from the materials under study.

Effect of time of carbonization on the properties of the adsorbents

Table 3 shows the effect of carbonization time on the properties of the adsorbents produced using H_3PO_4 as activating agent at 500 ^{o}C and 600 ^{o}C for TOSS and GASS, respectively. From the table, it can be seen that the bulk density and yield of the adsorbents decreased while surface area, total pore volume, weight loss and ash content increased with increase in carbonization time from 60 minutes to 180 minutes for both raw materials. This trend is attributable to the increased removal of volatile matter as a result of increase in thermal decomposition of the raw material as the carbonization time increased[36]. Increased activation temperature and time leads to the increased carbon and activation reagent reaction leading to increase in the degree of carbon burn-off and decrease in yield[37]. Since yield decreases with increase in carbonization time, it is therefore necessary to consider production losses in choosing the carbonization time for production of activated carbon, without necessarily compromising efficiency.

Table 3. Effect of carbonization time on properties of adsorbents produced using H_3PO_4 as activating agent at 500 ^{o}C for TOSS and 600 ^{o}C for GASS

Parameter	60, min		90, min		120, min		150, min		180, min	
	TOSS	GASS	TOSS	GASS	TOSS	GASS	TOSS	GASS	TOSS	GASS
Yield, %	48.06	64.91	45.75	60.01	40.17	55.82	37.75	51.86	35.58	44.37
Weight loss %	51.94	35.09	54.25	39.99	59.83	44.18	62.23	48.14	64.43	55.63
Surface area, m^2/g	875	837	919	887	937	906	963	942	1007	985
Total pore volume cm^3/g	2.77	2.65	3.10	2.97	3.52	3.23	3.72	3.45	3.92	3.54
Bulk density, g/cm^3	0.286	0.465	0.270	0.423	0.263	0.386	0.256	0.357	0.250	0.343
Ash content, %	3.40	2.45	4.60	3.95	5.15	4.90	5.60	5.30	6.35	5.50

A key property of activated carbons is their surface area[38]. Commercial activated carbons typically have a surface area in the range of 400-1500 m^2/g[39]. The ranges of surface area of the activated carbons produced in this work were well within the range reported in the literature for various precursors and comparable to the surface areas of some commercial activated carbons. It is obvious that the activated carbon from the different adsorbents exhibited a continuous increase in the total pore volume (micropores and mesopores) with increase in carbonization time over the whole duration of carbonization considered in the current work. This observation is in keeping with literature reports[38]. From Tables 1 to 3, it can be seen that the TOSS carbons had higher surface area, total pore volume, weight loss and ash content as well as lower bulk density and yield than the GASS carbons produced under the same experimental conditions. This may be attributed to higher thermal decomposition of TOSS than GASS since burn-off is dependent on the precursor material amongst other parameters.

Effect of activating agent on adsorption

Tables 4 show the effect of activating agent on GASS and TOSS, respectively, with respect to the quantity of Pb(II) adsorbed by each of the adsorbents.

**Table 4.** Effect of Activating Agent on Adsorption Parameters forGASS and TOSS*

Sample	C_e mg/ℓ		$C_o - C_e$ mg/ℓ		q mg/g		% q	
	GASS	TOSS	GASS	TOSS	GASS	TOSS	GASS	TOSS
H_3PO_4 Activation	147.00	109.25	53.00	90.75	10.60	18.15	26.50	45.38
NH_4Cl Activation	166.00	164.50	34.00	35.50	6.80	7.10	17.00	17.75
Raw Material[+]	188.00	185.00	12.00	15.00	2.40	3.00	6.00	7.50

C_o (mg/L) = 200; V (mℓ) = 100; m (g) = 0.5; C_o, C_e, V, m and q have same meaning as in Eq. 6;%q = percent of original concentration of metal ion adsorbed; GASS and TOSS carbonized at 600 and 500 ^{o}C, respectively.[+]unactivated but carbonized TOSS

The results show that the activated carbons adsorbed higher amounts of Pb(II) than the raw material (in the case of GASS) and the unactivated but carbonized TOSS (in the case of TOSS). The results also show that the AC produced by activation with H_3PO_4 adsorbed more Pb(II) ions than the ones produced by activation with NH_4Cl. As a result of this, activation with phosphoric acid was employed in the further production of the carbons for the rest of our work.

Effect of carbonization temperature on adsorption

Figure 1 shows the effect of carbonization temperature of the samples on their adsorption of Pb(II) ions. From the figure, adsorption increased as carbons produced at higher temperatures were used for both raw materials consistent with the data in Table 3[36].
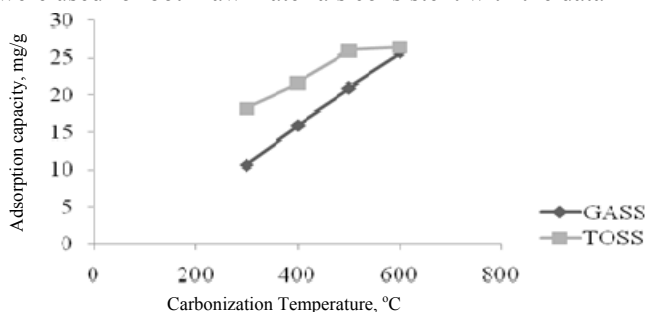
Figure 1. Effect of carbonization temperature on Pb(II) ions adsorption

The results also show that TOSS carbons adsorbed more of the metal ion than GASS carbons carbonized at the same temperature. This can be attributed to the possession of higher surface area and total pore volume by TOSS carbons than GASS carbons (Table 3). However, carbonization at 600°C resulted in marginal increase in the amount of lead adsorbed by TOSS. As a result of this and also taking production losses (in terms of % weight loss) into consideration, 500 ^{o}C was used for the further production of carbons from TOSS for the rest of the research while 600 ^{o}C was used for GASS.

Effect of carbonization time on adsorption

Figure 2 shows the effect of carbonization time of TOSS (at 500 ^{o}C) and GASS (at 600 ^{o}C) on their ability to adsorb Pb(II) ions from aqueous solution. For both raw materials, adsorption increased as carbons produced by carbonization for longer period of time were used.
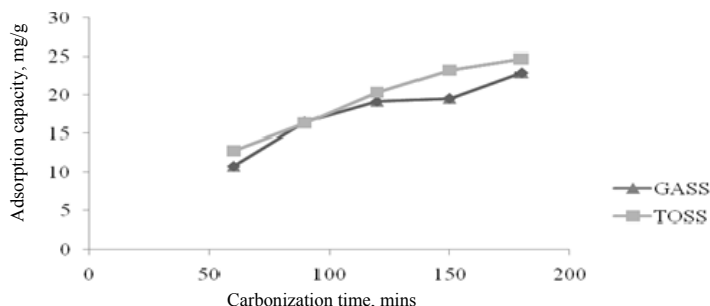
Figure 2. Effect of carbonization time on Pb(II) adsorption (500 ^{o}C for TOSS and 600 ^{o}C for GASS)

This is as a result of possession of higher adsorption properties by carbons produced by longer carbonization times as the burn-off and subsequent creation of more pores and adsorptive sites became higher[36].

From the results, it can also be seen that TOSS carbons adsorbed more of Pb(II) ions than GASS carbons carbonized for the same length of time. This is can be attributed to the possession of higher surface area and total pore volume by TOSS than GASS carbons at the same carbonization time (Table 4). However, carbonization for 150 and 180 minutes resulted in marginal increase in the amount of metal adsorbed by the carbons from both raw materials. As a result of this and also taking production losses (with respect to weight loss) into consideration, carbonization was done for 60 minutes and 120 minutes for TOSS and GASS, respectively in the further production of carbons for the rest of this report.

Effect of Adsorption Process Variables

Effect of contact time on adsorption

The effect of contact time on the adsorption of Pb(II) by both GASS and TOSS is shown in Figure 3. The removal of Pb(II) was faster and higher in the initial stages and decreased with time until equilibrium was attained as a result of decrease in available surface area as contact time increased[6]. The figure also reveals that the curves are smooth and continuous, leading to saturation, suggesting possible monolayer coverage of the metal ions on the carbon surface[40]. The results further show that the GASS carbon adsorbed more Pb(II) ions than the TOSS carbon. This could be attributed to the fact that GASS carbonized at 600 ^{o}C for 120 minutes possessed better adsorption properties (higher surface area and pore volume) than TOSS carbonized at 500 ^{o}C for 60 minutes as shown in Table 4.
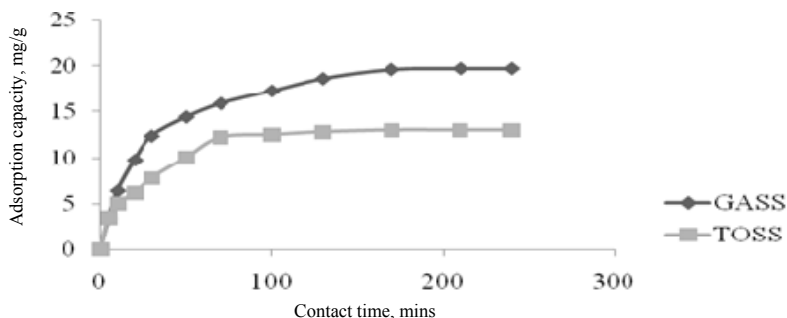

Figure 3. Effect of contact time on Pb(II) adsorption

It is seen that 3 hours was sufficient for the sorption equilibrium to be achieved as no further adsorption took place after 180 minutes.

Effect of initial Pb(II)Concentration on Adsorption

The effect of initial Pb(II) concentration on its adsorption by activated carbon from both GASS and TOSS is shown in Figure 4..
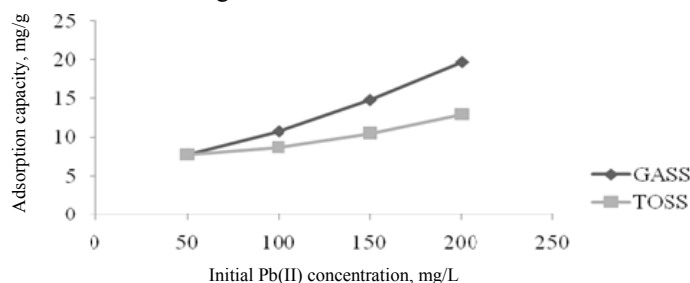

Figure 4. Effect of initial Pb(II) concentration on its adsorption

Adsorption increased with increase in the initial concentration of Pb(II) for both adsorbents. This is because increases in initial metal ion concentrations are effective to break the resistance originating from mass transfer, resulting in increased adsorption[41].

Effect of Solution pH

The effect of pH of Pb(II) solution on its adsorption by activated carbon from both raw materials is shown in Figure 5.
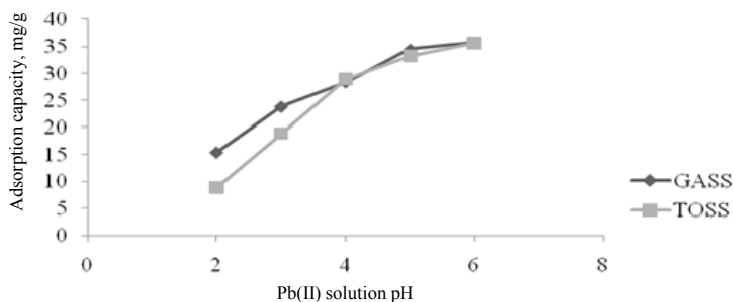

Figure 5. Effect of Pb(II) solution pH on its adsorption

From the figure, it can be observed that adsorption increased with increasing pH until pH of 6, when the Pb(II) ions were precipitated out of the solution. Hence, the experiment was terminated at pH value of 6. At very low pH values, the Pb(II) solution was rich in protons which occupy considerable sites on the adsorbent surface. As the pH increases, the competition is reduced, thereby facilitating the access of the sites to the Pb(II) ions, thus leading to a higher rate of retention. On further increase of the pH, the solubility of Pb(II) decreased so much that they were precipitated out of their solutions as lead hydroxide[16]. The Pb(II) ions in aqueous solution may undergo solvation, hydrolysis and polymerization as shown in Eqs. 7-9[15].

$$Pb^{2+} + nH_2O \rightleftarrows Pb(H_2O)_n^{2+} \tag{7}$$

$$Pb(H_2O)_n^{2+} \rightleftarrows Pb(H_2O)^{n-1}(OH)^+ + H^+ \tag{8}$$

$$nPb^{2+} + mH_2O \rightleftarrows Pb(OH)_m^{2n-m} + mH^+ \tag{9}$$

Pb^{2+} ion can form several hydrolysis products, which exist under different conditions. In dilute aqueous solutions of pH<6, lead ions exist as Pb^{2+} or $Pb(OH)^{+}$ or both, whereas the formation of Pb^{2+} hydrolysis products occur at pH>6.0,which might lead to its polymerization and consequent precipitation.

Effect of activated carbon particle size on adsorption

The effect of particle size of activated carbon from both GASS and TOSS on the adsorption of Pb(II) is shown in Figure 6.
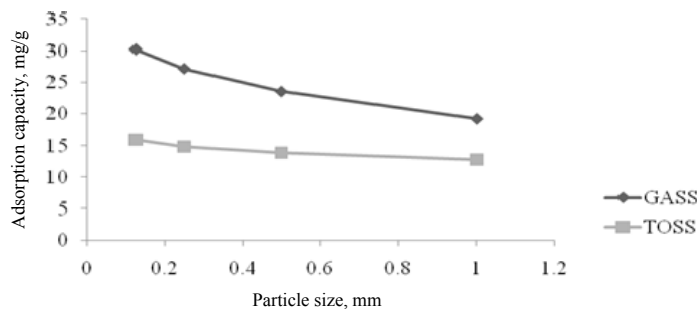

Figure 6. Effect of activated carbon particle size on Pb(II) adsorption

Adsorption decreased with increase in particle size of the activated carbons. This is because the effective surface area of activated carbons increases with decrease in particle size of the carbons[6-7,23].

Effect of activated carbon dose

The effect of the dose of activated carbon on the adsorption of Pb(II) ions from aqueous solution is shown in Figure 7. From Figure 7, it can be seen that the percentage removal of Pb(II) ions increased as the activated carbon dose increased in both cases. This increase in Pb(II) removal with increase in adsorbent dose is due to the greater availability of the exchangeable sites or surface area at a higher concentration of the adsorbent[15,17].
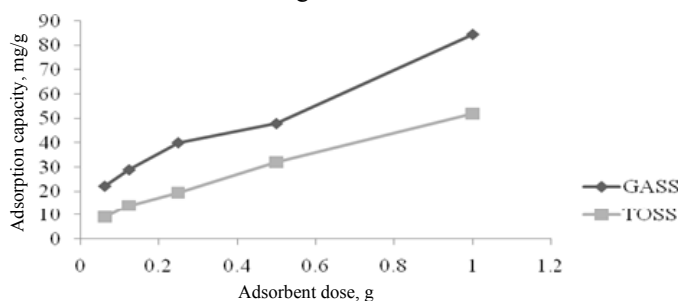

Figure 7. Effect of activated carbon dose on Pb(II) ions adsorption

However, the amount of adsorbed metal ion per gram (adsorption capacity) decreased with increasing biosorbent dose from 0.1 to 1.0 g because of unsaturation of adsorption sites through the adsorption process[42] or the concentration gradient between the adsorbent and the adsorbate[43].

The adsorption capacities of GASS and TOSS at 5 g/100 mLof solution and 200 mg/L of Pb^{2+} ions are 96 and 64 mg/g, respectively. The results obtained from the present study were compared with the results reported in literature in Table 5.

Table 7. Monolayer adsorption capacities of activated carbons derived from some lignocellulosic materials for lead(II) ions

S.No	Adsorbent Material	Adsorption capacity mg g^{-1}	Reference
1	Cocoa shells	6.23	44
2	Pomegranate peel	13.87	18
3	Apricot stone	22.85	8
4	Mango leaves	31.54	20
5	Sago wastes	46.6	23
6	Pecan shell	64.2	45
7	*Telfairiaoccidentalis*seed shells (TOSS)	64.0	Present work
8	Palm shell	95.20	22
9	*Gambeyaalbida*seed shells(GASS)	96.2	Present work
10	Mango peel waste	99.05	21
11	Cucumber peels	147.06	15
12	Pecan nutshell	195.9	24
13	*Euphorbia rigida*	279.72	19
14	Soybean oil cake	476.2	4

The adsorption capacity of Pb(II) ions by some of the plant materials in the table are found to be comparable to those of the present work, with some being either far lower or higher.

Effect of adsorption temperature

Temperature has a significant impact on the sorption process, resulting in varying contributions of individual sorption mechanisms to the overall process, involving the co-existence of physisorption, *i.e*., ion exchange, electrostatic attraction and chemisorption, *i.e*., surface complexation[46]. Seven characteristics which determine the adsorption mechanism, *i.e*., chemisorption or physisorption, are described in the literature. Generally, chemisorption is favoured at increased temperature and the opposite is true for physisorption[46]. The effect of adsorption temperature on the adsorption of Pb(II) by the activated carbons is shown in Figure 8. It is observed from the figure that the adsorption decreased as temperature increased.
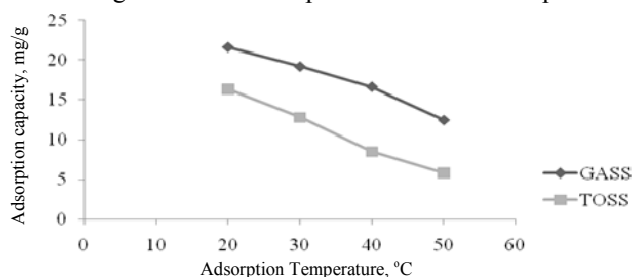
Figure 8. Effect of adsorption temperature on Pb(II) adsorption

With increasing temperature, the attractive forces between biomass surface and metal ions are weakened and the sorption decreases suggesting that the adsorption process with the adsorbents was exothermic as Dudareva *et al.*[47] had indicated that adsorption process is endothermic in nature if at increasing the temperature, the adsorption of metal ions by carbon materials becomes stronger.

Conclusion

The results of this research show that AC can be produced from *Gambeya albida* (GASS) and *Telfairia occidentalis* seed shells (TOSS) with H_3PO_4 had higher adsorption potentials than those of NH_4Cl. Increase in carbonization temperature and time yielded carbons with higher adsorption capacities. Activated carbons produced from TOSS have better adsorption properties than those produced from GASS under the same experimental conditions. Adsorption of Pb(II) by activated carbon from both seed shells is influenced by contact time, initial Pb(II) concentration, solution pH, activated carbon particle size and dose as well adsorption temperature. The results revealed that TOSS and GASS as ecofriendly waste materials, are promising and renewable low-cost adsorbents for removal of Pb(II) ions from aqueous solutions.

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