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CORRELATIVE STUDY OF LEAD ION REMOVAL EFFICIENCY FROM AQUEOUS SOLUTION USING ACTIVATED CARBONIZED AFRICAN STAR APPLE SEED COAT (*Chrysophyllum albidum)* AND ACTIVATED *Lophira alata* CARBONIZED SAWDUST

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ABSTRACT

Water is very useful to human existence. Lead accumulation along the food chain can result in serious health hazards. This research was designed to examine the removal efficiency of Pb^{2+} ion from aqueous solution using activated carbonized African star apple seed coat (ACASASC) and activated *lophira alata* carbonized sawdust (ALACS) obtained from Benin City, Edo State, Nigeria. The ACASASC and ALACS were prepared by carbonization and activated using KOH. ACASASC and ALACS were physicochemically characterized. The adsorption process of Pb^{2+} ions on ACASASC and ALACS was studied using the batch adsorption experiments and the data obtained were analyzed using adsorption isotherm model. The SEM picture, the iodine number and porosity determination revealed that ACASASC had a larger surface area than ALACS. FTIR spectrum revealed the ACASASC possessed higher amount of oxygen carrying functional groups compared to that of ALACS, indicating that the ACASASC possess higher adsorption capacity than ALACS. The quantity (q_m) of Pb^{2+} ions adsorbed by ALACS was lower compared to that of ACASASC. The adsorption process of Pb^{2+} ions onto ACASASC and ALACS was physical and spontaneous. The adsorption isotherm model revealed that ACASASC is a more efficient removal of Pb^{2+} ions from aqueous solution compared to ALACS.

Keywords: Carbonization, Activated, impregnate, Adsorption Isotherm.

INTRODUCTION

Water is an essential natural resource necessary for the survival of all living organisms, due to industrialization, the rate at which heavy metals bearing effluents are discharged into our environment and water bodies has increased rapidly (Babel *and* Kurniawan 2004), hence, the need to ensure the safety of our environment. Some of the major advantages of applying biosorbents or their derivative include competitive performance, heavy metal sensitivity, selectivity, cheapness and ease of generation, known process equipment, possible metal recovery and no sludge generation.

Although, several contaminants have been found in water, heavy metals pose more serious environmental threats. Heavy metals are metallic chemical elements that have a relatively high density and are toxic or poisonous at low concentrations. One major heavy metal of concern is Lead. Lead has been found to be extremely toxic and shows toxicity to vital parts of the body (Sabastine and Wendy, 2009). The effects of lead occur over a broad range of doses, causes problems in the synthesis of hemoglobin, effects on the kidney and gastro-intestinal tracts, joints and reproductive system; acute or chronic damage to the nervous system. It is also harmful to plant and aquatic life. (Agency for Toxic Substances and Disease Registry, 2007).

Several methods have been employed in the sequestration or removal of heavy metal ions from aqueous solution, most of these methods have been found to be capital intensive, result in formation of sludge, sensitive to toxic substances and unfriendly to the environment (Adeyemo *et al.*, 2014; Shrimant *et al.*, 2015).

The maximum concentration limit for lead ions in drinking water has been strictly regulated. The World Health Organization (WHO) set a maximum guideline concentration of 0.01 mg/L for Pb^{2+} ions in drinking water (WHO, 2008). It has been confirmed that the removal of Pb^{2+} ions is more at pH 5.0-8.0 (Malik *et al.*, 2015).

The motivating factors in the use of activated carbonized African star apple seed coat (ACASASC) and activated *lophira alata* carbonized sawdust (ALACS) in removing lead ions from aqueous solution include, the abundance of their biomass waste and consequent reduction in the cost of operation compared with the use of conventional adsorbents, as well as the reduction or elimination of the nuisance caused by the biomass waste.

MATERIALS AND METHODS

Sample Collection

African star apple seed coat used as the precursor for the preparation of activated carbon was obtained from the African star apple fruits purchased from New Benin market, Benin City, Edo state and the *Lophira alata* sawdust was collected from a saw mill located in Akpata axis along Upper Siluko road, Egor Local Government area, Benin City, Edo State. The sawdust was collected into polythene bag attached to the machine while in operation to avoid collecting contaminated sawdust. The African star apple fruits and lophira alata wood and leaves were identified by expert in the field of Forestry from the Department of Forestry and Wildlife, University of Benin, Benin City, Nigeria.

Preparation of Activated Carbonized African Star Apple Seed Coat (ACASASC) and Activated *lophira alata* carbonized sawdust (ALACS)

The brown seed coats obtained from the African Star Apple fruits were cracked open to remove its soft whitish inner contents. The hard-brown seed coats were crushed, and the crushed seed coats obtained was washed thoroughly with distilled water to remove any surface impurities, and then sun dried for 7 days to remove moisture. The dried crushed African star apple seed coats were ground and carbonized in a clay pot placed in a muffle furnace (Uniscope SM9080) and heated at a temperature of 300℃ for 2 hours. The carbonized African Star Apple seed coats were sieved using 300µm mesh sieve (BSS 052). The *lophira alata* sawdust was carbonized in same manner. The sieved carbonized African star apple seed coats and the carbonized *Lophira Alata* sawdust were impregnated with Potassium hydroxide (KOH) with an impregnation ratio of 1:1 in separate containers for 48 hours until their mixture turned into a paste. This was done to open the pores and optimize the properties of the carbon. KOH was a more preferable activation agent because it is a strong dehydrating agent and it alters the carbon to form porous structure (Grigis *et al*., 1999). The KOH impregnated carbonized African star apple seed coats and the carbonized *Lophira Alata* sawdust was separately filtered and oven dried at 105℃ for 6 hours. After oven drying them, they were reintroduced into the Muffle furnace and heated at 300℃ for 1 hour. The ACASASC and ALACS were washed with distilled water until the pH of the filtrate was∼7. The residue (ACASASC and ALACS) was then dried at 105℃ for 6 hours, the ACASASC and ALACS was allowed to cool and were stored in different airtight container for further use.

Adsorbates Preparation and Characterization

An aqueous solution of Pb^{2+} ion (adsorbate) was prepared from lead nitrate salts obtained from BDH chemicals of analytical grades and its actual concentrations confirmed with atomic absorption spectrophotometer (AAS).

Physicochemical Characterization of ACASASC and ALACS

The physicochemical characterization of the ACASASC and ALACS was done using scanning electron microscope (SEM; phenom pro suite desktop scanning electron microscope) to view images which reveals their morphologies, Fourier-transform infrared spectrophotometer to determine the functional groups present in the ACASASC. ACASASC were also characterized for pH, iodine value, ash content and moisture content.

Adsorption Isotherm Studies

The effect of adsorbent dose, time, and pH on the removal of Pb^{2+} ions were investigated. The adsorption process of Pb^{2+} ion onto ACASASC and ALACS was studied using the batch adsorption experiments. The equilibrium concentration of the metal ions in the treated samples was determined using atomic absorption spectrophotometer (Buck scientific model VGP-210).

Adsorption Isotherm Model

Information on the affinity between the adsorbent-adsorbate, adsorption capacity of the adsorbent, surface area, porosity and adsorption heat can be obtained from adsorption isotherms models (Yildiz, 2017). The equilibrium amount of adsorbate adsorbed (or adsorption capacities) and adsorption efficiency from the aqueous solution were calculated using equation 1 and 2 respectively:

$$q_e = \frac{(C_o - C_e)v}{M} \quad \text{(Kocaoba et al., 2007) (1)}$$

$$\%E = \frac{C_o - C_e}{C_o} \times 100 \quad \text{(Kocaoba et al., 2007) (2)}$$

Where q_e is the amount of adsorbate adsorbed at equilibrium (mg/g); C_0 is the initial concentration of adsorbate (mg/l); C_e is the equilibrium concentration of adsorbate (mg/l) left in solution; M is the adsorbent mass (g); and V is the volume of the aqueous solution (l).

The data obtained from the adsorption study were analyzed using the Langmuir, Freundlich, Dubinin-Radushkevick (DRK) and Flory-Huggins adsorption isotherm model. The Freundlich, Dubinin-Radushkevick and Flory-Huggins adsorption isotherm model are given respectively by equations (3), (4), (5) and (6).

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_l q_m C_e}$$ (Sarma *et al.*, 2015) (3)

$$\log q_e = \mathrm{loqk_f} + \left(1/n_f\right)\mathrm{logC_e}$$ (Norasiha *et al.*, 2016) (4)

$$\mathrm{lnq_e} = \mathrm{lnq_m} - \beta.\varepsilon^2$$ (Ebrahimian *et al.*, 2016) (5)

$$[\varepsilon = \mathrm{RTln}(1+1/C_e)]$$ (5a)

$$E = 1/(-2\beta)^{1/2}$$ (5b)

$$\mathrm{Log}\ (\theta/C_o) = \mathrm{Log}\ K_{FH} + n\ \mathrm{Log}\ (1-\theta)$$ (Nechifor *et al.*, 2016) (6)

$$[\theta = (1- [C_e/C_0])]$$ (6a)

These adsorption isotherms models were considered so as to compare the adsorption mechanism and adsorption strength, $(1/n_F)$, adsorption intensity (n_F), the average free energy of the adsorption per molecule of the adsorbate when it is transferred to the surface of the adsordent from infinity in solution (E), the adsorption process type - whether physical or chemical (ion exchange) adsorption mechanism (if E is between 8-16kJ/mol it is chemical sorption and if lower than 8kJ/mol it is physical sorption), adsorption limit (q_m), their adsorption capacity (k_F) , the degree of adsorbate occupying the adsorption site (k_{FH}), the spontaneity of adsorption and the heat of adsorption type (ΔG^o_{FH}) between the adsorbent (ACASASC and ALACS) and adsorbate (Pb^{2+} ions) (Mekonnen *et al.*, 2015; Nechifor *et al.*, 2015;Tajun *et al*, 2016; Ebelegi *et al.*, 2017).

RESULTS

Physicochemical Characteristics of the ACASASC and ALACS

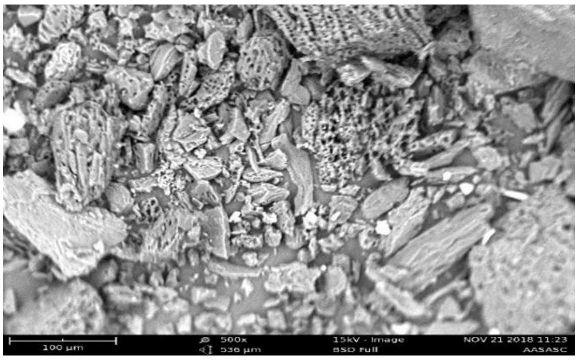
Physicochemical characteristics of the ACASASC and ALACS used for adsorption studies of lead ion from aqueous solution are shown in the Table 1 below.

Table 1: Physicochemical characteristics of the ACASASC and ALACS

Parameters	ALACS	ACASASC
PH	7.00	6.72
Moisture content (%)	2.98	2.17
Ash content (%)	5.10	2.23
Bulk density (g/cm^3)	0.35	0.48
Particle density (ml/g)	0.52	0.45
Pore volume (cm^3/g)	1.92	2.22
Iodine value (mg/g)	680.25	760.40
Particle size (µm)	≤ 300	≤ 300

Scanning Electron Microscopy (SEM)

The morphology of the prepared ACASASC and ALACS is shown in Figure 1 and 2.



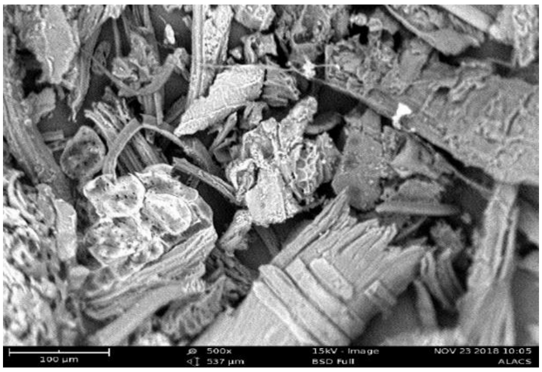


Figure 1: SEM image of ACASASC

Figure 2: SEM image of ALACS

Fourier Transformed Infrared Spectroscopy (FTIR)

The Fourier Transform Infrared Spectrum of the prepared ACASASC and ALACS are shown in Figure 3.

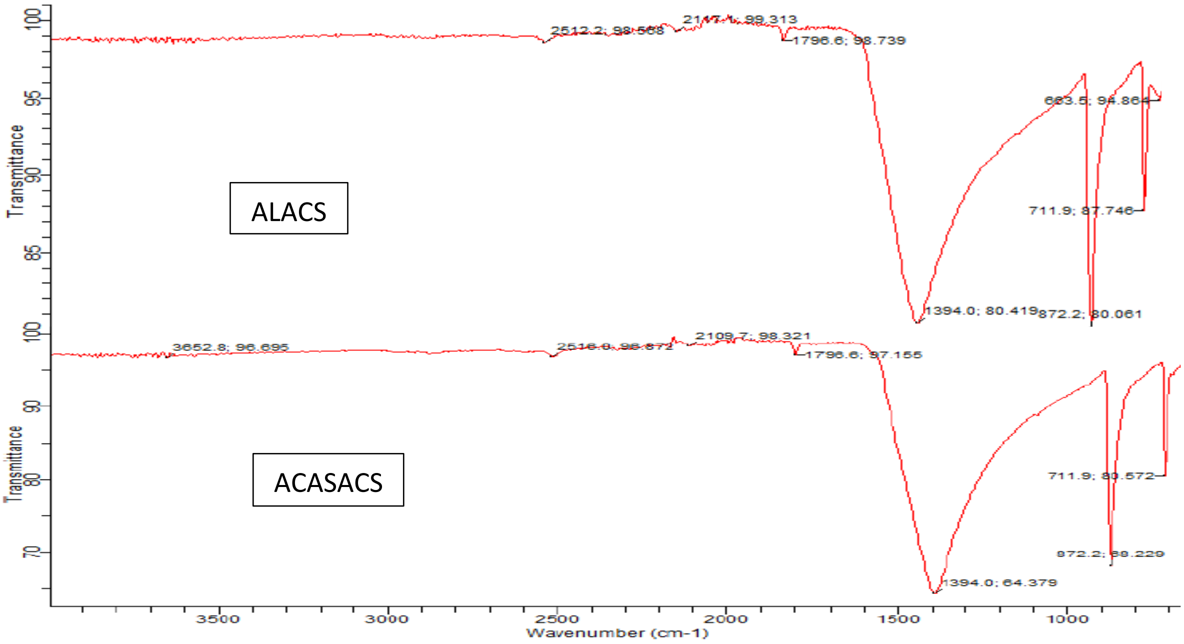


Figure 3: Fourier Transform Infrared Spectrum of ALACS and ACASASC

Results for the Adsorption of Lead Ions on ALACS and ACASASC

The representative graphs for the adsorption isotherm model and the values obtained from the isotherm models' parameter for adsorption of Pb^{2+} ions onto ALACS and ACASASC are shown in Figure 4, 5, 6, 7 and Table 2.

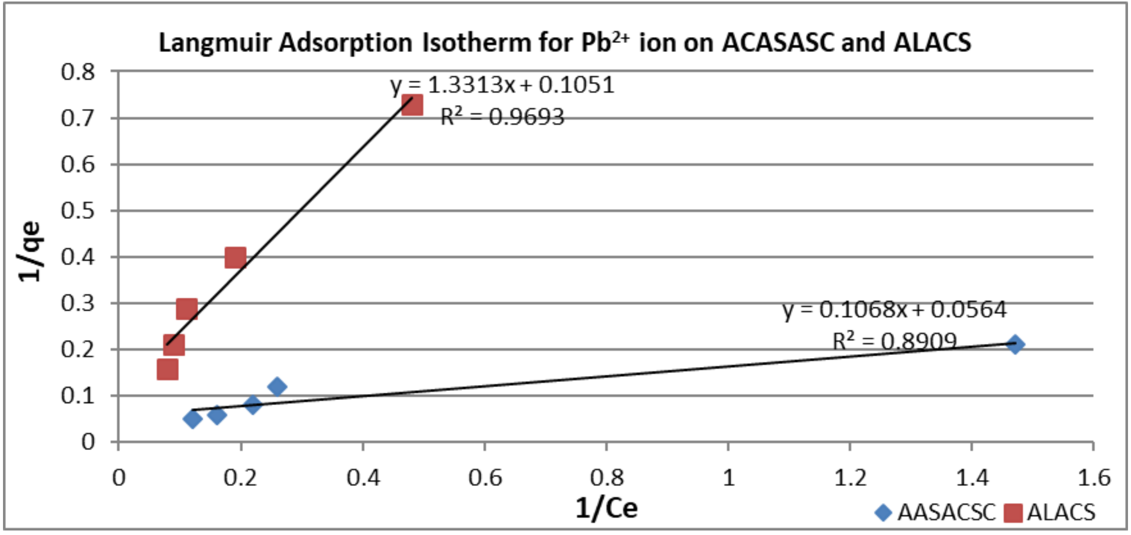


Figure 4: Langmuir Adsorption Isotherm for the sorption of Pb^{2+} on ALACS and ACASASC

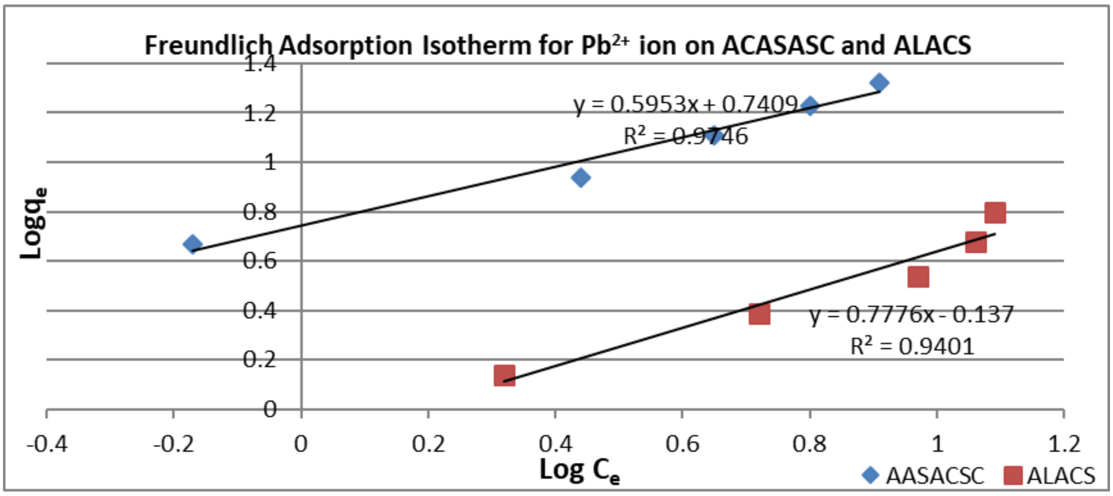


Figure 5: Freundlich Adsorption Isotherm for the sorption of Pb^{2+} on ALACS and ACASASC

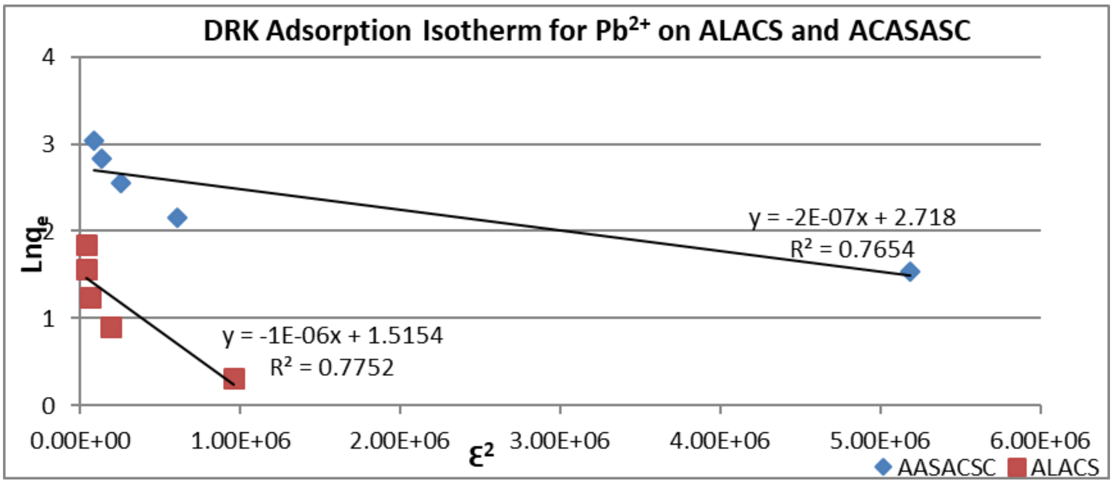


Figure 6: DRK Adsorption Isotherm for the sorption of Pb^{2+} on ALACS and ACASASC

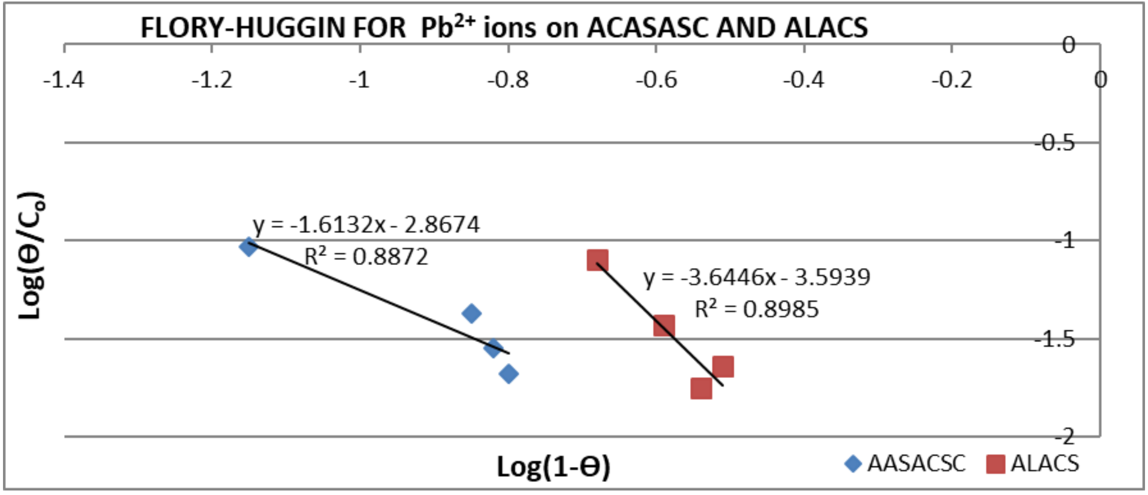


Figure 7: Flory-Huggin Adsorption Isotherm for the sorption of Pb^{2+} ions on ALACS and ACASASC

Table 2: parameters of Adsorption isotherm models for adsorption of Pb^{2+} ions onto ALACS and ACASASC

Adsorption Isotherm Model	Parameters	Units	AASACSC	ALACS
Langmuir	$\mathbf{R^2}$		**0.89**	**0.97**
$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_l q_m C_e}$	$\mathbf{q_m}$		**17.73**	**9.51**
	$\mathbf{k_L}$		**0.53**	**1.00**
Freundlich	R^2	-	0.97	0.94
$\log q_e = \mathrm{loqk_f} + (1/n_f)\log C_e$	K_F	L/mg	5.51	0.73
	n_F	-	1.68	1.29
Dubinin-Radushkevick	R^2	-	0.77	0.78
(DRK)	q_m	mg/g	15.15	4.55
$\ln q_e = \ln q_m - \beta . \varepsilon^2$	B	mol^2/J^2	-2.00×10^{-7}	-1.00×10^{-6}
$[\varepsilon = RT\ln(1+1/C_e)]$	E	kJ/mol	1.58	0.71
Flory-Huggins	R^2	-	0.89	0.90
$\text{Log}(\theta/C_o) = \text{Log } K_{FH} + n \text{ Log}$	K_{FH}	$Lmol^{-1}$	1.36×10^{-3}	2.55×10^{-4}
$(1-\theta)$	n_{FH}	-	-1.61	-3.64
$[\theta = (1- [C_e/C_0])]$	ΔG	KJ	-16.63	-20.84

DISCUSSION

Physicochemical Characteristics of the ACASASC and ALACS

Both pH of the ACASASC and ALACS in Table 1, fell within the pH range of 6-8 for carbons useful in most applications for the adsorption of heavy metals from aqueous solution (Okieimen *et al.*, 1999). This implies that the pH of the ACASASC and ALACS is acceptable for applications involving adsorption of heavy metals from aqueous solution.

The iodine value obtained indicated that the ACASASC has a higher surface area for adsorption than ALACS. Iodine adsorption is a simple and quick technique to determine the adsorptive capacity of activated charcoal, also known as iodine number, often reported in mg/g. It has been established that the iodine number gives an estimate of the surface area and is related to the porosity characteristics of the activated charcoal (Khadija *et al*., 2015; Ghogomu *et al.,* 2016). The ash content shows the amount of inorganic substituent present in the carbon. From the characterization, it was observed that the ACASASC had less ash content which is desirable for activated carbon (Table 1). High ash content is undesirable for activated carbon because it reduces the mechanical strength of carbon and affects adsorptive capacity.

Scanning Electron Microscopy (SEM)

The SEM photograph revealed that ACASASC posesses a variety of larger number of open pores of varied size compared to that of ALACS (Fig 2 and 3). The SEM image also show that the particles consist of pores having irregular shapes. The fragmention of the particles and the difference in pore size depicts the differences in physical characteristics between the ACASASC and ALACS resulting from the KOH activation. This difference in pore size is an indication that the ACASASC will be a better adsorbent for Pb^{2+} ions in aqueous solution than ALACS, this corresponds to the difference in porosity of the adsorbent (ACASASC and ALACS, Table 1)

Fourier Transformed Infrared Spectroscopy (FTIR)

The Fourier Transform Infrared Spectrum of ALACS and ACASASC showed similar characteristic bands at 711.9 cm^{-1} for IR absorption of aromatics for 5-adjacent H, monosubstituted aromatics; 872.2 cm^{-1} represents IR absorption of aromatics for isolated H, metadisubstituted aromatics; 1394.0 cm^{-1} represent a C-H bending for tertiary butyl group; 1796.6 cm^{-1} represents C=O stretching for anhydride $R(CO)_2O$, it also indicated the presence of 5-membered cyclic saturated acid anhydride and saturated acid chloride. The ALACS exhibited a distinct characteristic absorption band at 2512.2 cm^{-1} representing broad -OH stretch for carboxylic acid (-COOH) and at 663.5 cm^{-1} that indicated –C-H bending vibration of acetylene or monosubstituted acetylenes, while the ACASASC revealed a distinct characteristic absorption band peak at 3652.8 cm^{-1} depicting the presence of O-H stretch for alcohol (ROH) and phenol (ArOH) and at 2516.0 cm^{-1} revealing broad -OH stretch for carboxylic acid (-COOH) (Fig. 4). The IR absorption of ACASASC and ALACS at 2109.7 cm^{-1} and 2117.1 cm^{-1} respectively, represented bonds for –N-C=S for isothiocyanate compounds and -C≡C- stretching of acetylinic molecule.

The ACASASC possessed higher amount of oxygen carrying functional groups compared to that of ALACS, this was due to the effect of KOH during activation process. According to Mohammad-Khah and Ansari (2009), all activated carbon retains some quantities of chemically bonded oxygen and hydrogen in the form of various functional groups that usually gives acidic character to carbon. The higher the amount of oxygen and hydrogen chemically bonded to the adsorbent surface, the higher its adsorption capacity. The FTIR spectrum in Figure 4 revealed that the ACASASC contains more oxygen and hydrogen atoms chemically bonded to its surface compared to ALACS FTIR spectrum. This indicated that the ACASASC has a higher adsorption possibility and capacity ALACS.

Results for the Adsorption Study of Lead Ions on ALACS and ACASASC

High correlations with a regression coefficient (coefficient of determination R^2) ranging from 0.76 to 0.97 were obtained when the representative graphs for the adsorption isotherm models were subjected to regression model analysis. The values obtained indicates that the sorption data can be described using the models (Fig. 5, 6, 7, 8 and Table 2).

The values of K_F, n_F from the Freundlich adsorption isotherm model in Table 2 revealed that the ACASASC had a stronger adsorption capacity, adsorption strength and higher adsorption intensity than ALACS. This is an indication that ACASASC form relatively stronger bonds between itself and the Pb^{2+} ions. The maximum adsorption value (q_m) from Dubinin-Radushkevick (DRK) and Langmuir adsorption isotherm model, revealed that ACASASC adsorbed Pb^{2+} ions more than the ALACS, an implication that ACASASC had a larger surface area than ALACS, this is in agreement with the iodine value observed in their physicochemical characterisation in (Table 1).

Furthermore, the k_{FH} value revealed that the Pb^{2+} ions occupying the ACASASC adsorption site is higher compared to ALACS. The values of ΔG obtained were negative an indication that the adsorption process was spontaneous (Table 1). However, the transfer of Pb^{2+} ions onto ACASASC surface is more spontaneous compared to ALACS based on the fact that the average free energy of adsorption per molecule (β) and (ΔG) for ALACS is higher than ACASASC (Table 2). The process of adsorption of Pb^{2+} ions onto ACASASC and ALACS was a physical process based on the fact that their values of energy of adsorption (E), were lower than 8kJ (Table 2).

CONCLUSION

Lead ion contaminated water can be very harmful to humans, hence the need for a cheap and affordable adsorbent prepared from convertible organic waste. Both ACASASC and ALACS could adsorb Pb^{2+} ions, however, ACASASC adsorbed Pb^{2+} ions onto it surface better than ALACS. The adsorption process of Pb^{2+} ions onto ACASASC and ALACS was physical and spontaneous. The ACASASC had a stronger adsorption capacity, adsorption strength and higher adsorption intensity than ALACS. ACASASC is a better adsorbent material that can efficiently remove of Pb^{2+} ions from aqueous solution compared to ALACS because of it better adsorption quality.

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