

Removal Efficiency for Lead Ions from Aqueous Solution Using Carbonized and Activated Carbonized Mango Seed Shell (*Mangifera indica*) from Benin City, Edo State, Nigeria.

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Abstract

Water is a very important component of the human body, without it, the human system cannot function effectively. Lead is non-biodegradable and can accumulate along the food chain which results in serious ecological and health hazards. This study was designed to evaluate the removal efficiency of Pb^{2+} ions from aqueous solution using carbonized and activated carbonized mango seed shell obtained from Benin City, Edo State, Nigeria. The adsorbent ACMSS and CMSS were prepared by carbonization in a muffle furnace at $250^{\circ}C$ for 2 hours and the carbon was activated using KOH with an impregnation ratio of 1:1 For 48 hours. The ACMSS and CMSS were physiochemically characterized using scanning electron microscope, Fourier-transform infrared spectrophotometer, pH, iodine value, porosity, ash content and moisture content. The adsorption process of Pb^{2+} ions on ACMSS and CMSS was studied using the batch adsorption experiments. The data obtained from the adsorption study were analyzed using the Freundlich, Dubinin-Radushkevich (DRK) and Flory-Huggins adsorption isotherm model. The iodine number determination, porosity determination and the SEM picture revealed that ACMSS had a larger surface area than CMSS, an indication that the KOH activation opened up the pore of the ACMSS. FTIR spectrum revealed that the ACMSS had a higher adsorption capacity than CMSS. The coefficient of determination, R^2 , ranging from 0.50 to 1.00 was obtained. The quantity (q_m) of Pb^{2+} ions adsorbed by CMSS (10.87mg/g) was lower compared to that of ACMSS (11.00) as obtained from DRK model. The adsorption of Pb^{2+} ions on the CMSS and ACMSS surface was a physical process and spontaneous. The ACMSS and CMSS are good materials that can be effectively used as an adsorbent for the removal of Pb^{2+} ions from aqueous solution, however ACMSS is better.

Keywords: Carbonization, Activated, impregnation, Adsorption Isotherm.

INTRODUCTION

Water is a very important component of the human body, without it, the human system cannot function effectively. Discharge of industrial effluents containing heavy metals into water bodies has brought about serious problems to the wellbeing and economy of the nation.

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Heavy metal pollution is of a major global concern. Heavy metals are generated and dispersed into our environment by human activities and once released into the environment these metals are recalcitrant. They bioaccumulate and do not change from their harmful state into harmless end products, thereby posing several health problems for animals, plants and human beings, thus, are dangerous pollutants to human and its environment (Malik *et al.*, 2015).

Unlike organic pollutants, heavy metals do not biodegrade. Lead for example is non-biodegradable and can accumulate along the food chain which results in serious ecological and health hazard. Lead causes damage to the brain, kidney, miscarriage in pregnant women, damage to organ for sperm production in men and death (Sabastine and Wendy, 2009). 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 use of agricultural waste as adsorbent does not in any way lead to loss of valuable nutrient rather it lead to the reduction of the menace caused by indiscriminate disposal of spoil mangoes and mango seed (Adeyemo *et al.*, 2014). Adsorption methods for remediation of heavy metals in contaminated water is simple in design, sludge-free, less capital intensive, insensitive to toxic substances and friendly to the environment (Adeyemo *et al.*, 2014; Shrimant *et al.*, 2015).

This study was designed to evaluate the removal efficiency of Pb^{2+} ions from aqueous solution using an inexpensive sorbent material such as carbonized and activated carbonized mango seed shell obtained from Benin City, Edo State, Nigeria.

MATERIALS AND METHOD

The materials used for this research work include: mango fruits, distilled water, analytical grade of lead nitrate and potassium hydroxide from BDH chemicals.

Collection of Samples

Mango fruits were purchased from Uselu Market, Egor local Government area Benin city, Edo state.

Preparation of Carbonized Mango Seed Shell (CMSS)

The fleshy part of the mango fruits was removed and the seed shell was cut open to remove its inner contents. The seed shell obtained was thoroughly washed with distilled water to remove any surface impurities, and then sun dried for 7 days to remove moisture. The dried seed shell was cut into smaller sizes with the use of a knife. The dried mango seed shell was placed in a clay pot and heated at a temperature of 250°C for 2 hours in a muffle furnace (Uniscope SM9080).

Activation of the carbonized Mango Seed Shell (ACMSS)

The carbonized mango seed shell was ground and sieved using 300 μ m mesh sieve (BSS 052). The sieved CMSS was impregnated with Potassium hydroxide (KOH) with an impregnation ratio of 1:1 for 48 hours until the mixture turned into a paste. This was done to increase the surface area and porosity of the activated carbon. KOH is a more preferable activation agent because it is a strong dehydrating agent and it alters the carbon to form porous structure. The sieved, KOH impregnated CMSS was washed with distilled water until the pH of the filtrate was 7. The activated carbonized mango seed shell was oven dried at 105°C for 6 hours to

prevent the interference of moisture and the ACMSS was reheated in a muffle furnace at 250°C for 1 hour.

Adsorbates Preparation and Characterization

An aqueous solution of Pb²⁺ ion (adsorbate) was prepared from lead nitrate salts obtained from BDH chemicals of analytical grades and the concentration of the solutions prepared was confirmed with the use of atomic absorption spectrophotometer (AAS - Buck Scientific model VGP 210).

Physicochemical Characterization of ACMSS and CMSS

The physicochemical characterization of the ACMSS and CMSS 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 ACMSS and CMSS. The ACMSS and CMSS 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 Pb²⁺ ions was investigated. The adsorption process of Pb²⁺ ion onto ACMSS and CMSS was studied using the batch adsorption experiments. The batch adsorption experiments were conducted by varying Adsorbent dosage from 0.1g to 0.5g, contact time from 20min. to 100min. and pH from 3 to 7 at constant concentration of Pb²⁺ ion of 50 mg/l. Initial concentrations of Pb²⁺ ion was varied from 10 mg/l to 50 mg/l, at optimum ACMSS and CMSS doses, contact time, pH and agitation speed of 300 rpm. The equilibrium concentration of the Pb²⁺ 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:

$$q_e = \frac{(C_0 - C_e)V}{M} \quad (\text{Erdem, 2004}) \quad (1)$$

$$\%E = \frac{C_0 - C_e}{C_0} \times 100 \quad (\text{Erdem, 2004}) \quad (2)$$

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 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) and (5).

$$\log q_e = \log k_f + (1/n_f) \log C_e \quad (\text{Norasiha et al., 2016}) \quad (3)$$

$$\ln q_e = \ln q_m - \beta \cdot \varepsilon^2 \quad (4)$$

$$[\varepsilon = RT \ln(1 + 1/C_e)] \quad (4a)$$

$$E = 1/(-2\beta)^{1/2} \quad (\text{Ebrahimian et al., 2016}) \quad (4b)$$

$$\text{Log} (\theta/C_0) = \text{Log} K_{FH} + n \text{Log} (1-\theta) \quad (5)$$

$$[\theta = (1 - [C_e/C_0])] \quad (\text{Nechifor et al., 2016}) \quad (5a)$$

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 adsorbent 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°_{FH}) between the adsorbent (ACMSS and CMSS) and adsorbate (Pb^{2+} ion) (Mekonnen *et al.*, 2015; Nechifor *et al.*, 2015; Tajun *et al.*, 2016; Ebelegi *et al.*, 2017).

RESULTS AND DISCUSSION

Physiochemical Properties of ACMSS and CMSS

The values of the physiochemical characterization of ACMSS and CMSS are shown in table 1:

Table 1: Physiochemical Properties of ACMSS and CMSS

Parameters	CMSS	ACMSS
Moisture content (%)	2.59	0.53
Ash content (%)	1.92	1.92
Bulk density (g/cm ³)	0.49	0.50
Porosity	0.76	0.90
Iodine value (mg/g)	589.18	615.20
Particle density (ml/g)	2.03	5.02
pH	6.04	6.91
Particle size (μ m)	300	300

The pH of the ACMSS was close to neutral and CMSS was slightly acidic (Table 1). Carbons of pH range 6-8 are useful for most applications of adsorption (Okieimen *et al.*, 1991). Since the pH of these ACMSS and CMSS fell within this range, it was considered applicable in the adsorption of Pb (II) ions from aqueous solution.

Iodine adsorption determination was used to determine the adsorptive capacity of ACMSS and CMSS, the value obtained is referred to as iodine number often reported in mg/g (typical range 500-1200mg/g), the iodine number gives an estimate of the active surface area in mg/g present on the activated carbon and a measure of the micropore content of the activated carbon (Daniel *et al.*, 2017; Kulbir and Sadiq, 2019). The micropores areas are responsible for the large surface area of the activated carbon particle, created during activation process. ACMSS had a slightly higher iodine number hence more micropore thus a larger surface area than CMSS, and is related to the porosity characteristics of the adsorbent. A lower iodine number can be due to the presence of pores narrower than 1.0nm (Ghogomu *et al.*, 2016). The slight difference in iodine value indicates that the KOH activation did not effectively open up the pore of the ACMSS. The ash content shows the amount of inorganic constituent present in the carbon, high ash content is undesirable for carbon since it reduces the mechanical strength of carbon and affects its adsorptive capacity (Ukiwe *et al.*, 2008). The ash content of ACMSS and CMSS were the same and low, an indication that they both contain the same amount of inorganic constituents and their mechanical strength was desirable.

Scanning Electron Microscopy (SEM)

The SEM photograph at 1500 times magnification, revealed that ACMSS possesses a variety of larger number of open pores of varied size compared to that of CMSS (Fig 2 and 3). The SEM

image also show that the particles consist of pores having irregular shapes. The fragmentation of the particles and the difference in pore size depicts the differences in physical characteristics between the ACMSS and CMSS resulting from the KOH activation. This difference in pore size is an indication that the ACMSS will be a better adsorbent for Pb^{2+} ions in aqueous solution than CMSS, this corresponds to the difference in porosity of the adsorbent (ACMSS and CMSS, Table 1)

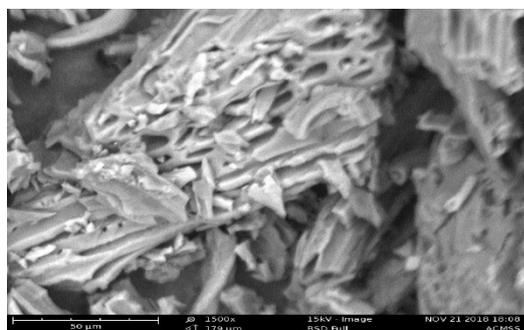


Fig 2: SEM image of ACMSS

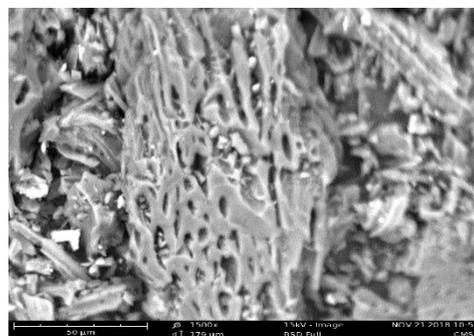


Fig 3: SEM image of CMSS

Fourier Transformed Infrared Spectroscopy (FTIR)

The Fourier Transform Infrared Spectrum of ACMSS showed characteristic bands at 3056.4 cm^{-1} which falls within frequencies representing N-H band for primary and secondary amines ($R-NH_2$ and R_2-NH), O-H stretch for carboxylic acid ($R-C=O$) and C-H stretch of $=C-H$ for alkenes and arenes. A characteristic band at 1949.4 cm^{-1} represents $C=C=C$ stretching of allenes. The peak at 1808.4 cm^{-1} represent a C=O stretch for acid anhydride and acid halide. A band at 1591.6 cm^{-1} represents C=C stretching for aromatics and N-H band of amine and amide. 1256.1 cm^{-1} represents C-O stretching of acid, esters and anhydrides. The peak at 1226.3 cm^{-1} corroborated the C-O stretch for acid, esters and anhydrides. The peak at 1174.1 cm^{-1} revealed the presence of C-O stretch for acids, esters and anhydride (Fig. 4).

The Fourier Transform Infrared Spectrum of CMSS showed characteristic bands at 1982.9 cm^{-1} and 2108.7 cm^{-1} represented bonds for $-N-C=S$ for isocyanate compounds. A peak at 1796.6 cm^{-1} represented bonds for C=O stretch for saturated acid anhydride ($R(COO)_2O$). The peak at 711.9 represented a C-H bend for monosubstituted benzene (Fig. 4).

The ACMSS possessed higher amount of oxygen carrying functional groups compared to that of CMSS, this was due to the effect of KOH during activation process. According to Mohammad-Khah and Ansari (2009), all activated carbon possess some amounts 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 ACMSS contains more oxygen and hydrogen atoms chemically bonded to its surface compared to CMSS FTIR spectrum. This indicates that the ACMSS has a higher adsorption capacity CMSS.

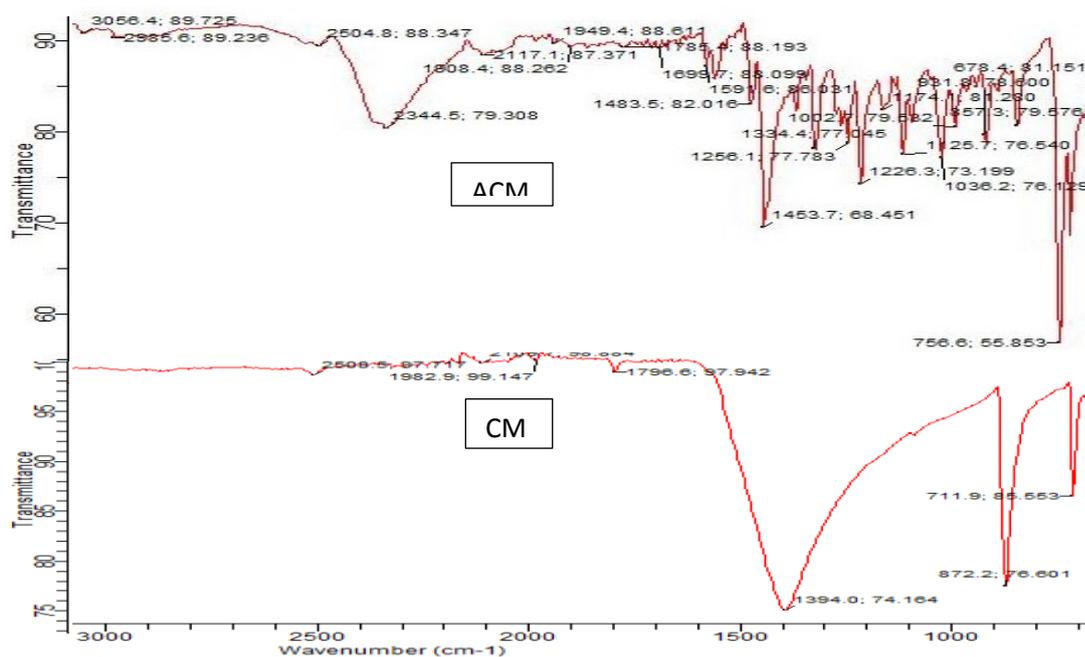


Fig 4: Fourier Transform Infrared Spectrum of ACMSS and CMSS

Results for the Adsorption of Lead Ion on ACMSS and CMSS

The representative graphs for the adsorption isotherm models obtained were subjected to regression model analysis. A high correlation coefficient (R) of between 0.50 to 1.00 regression coefficient (coefficient of determination, R^2) were obtained and this is an indication that the sorption data obtained can be described using the models (Fig. 5, 6, 7 and Table 2)

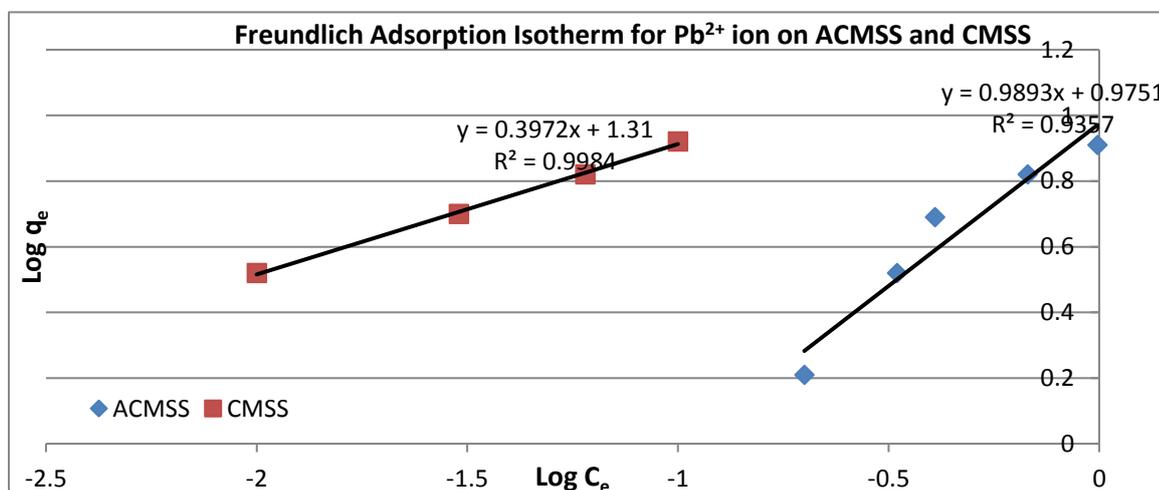


Fig. 5: Freundlich Adsorption Isotherm for the sorption of Pb^{2+} on ACMSS and CMSS

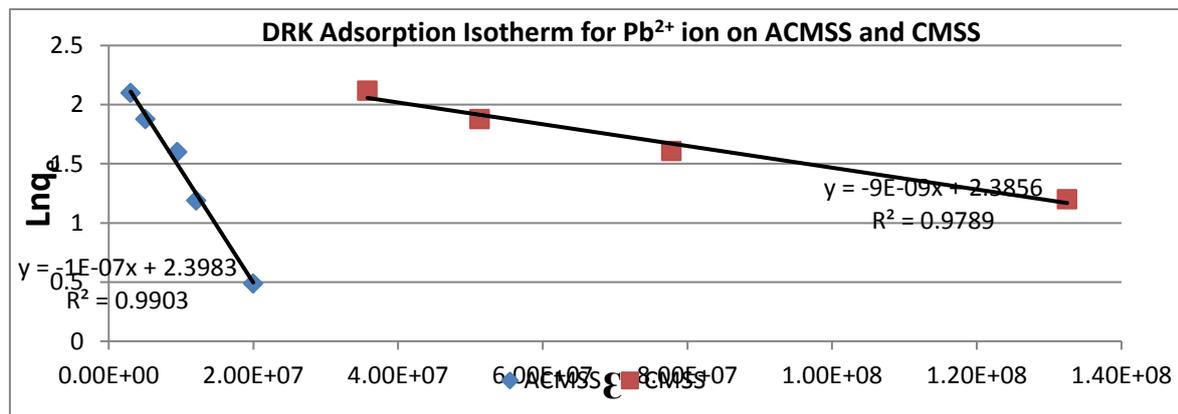


Fig. 6: DRK Adsorption Isotherm for the sorption of Pb^{2+} on ACMSS and CMSS

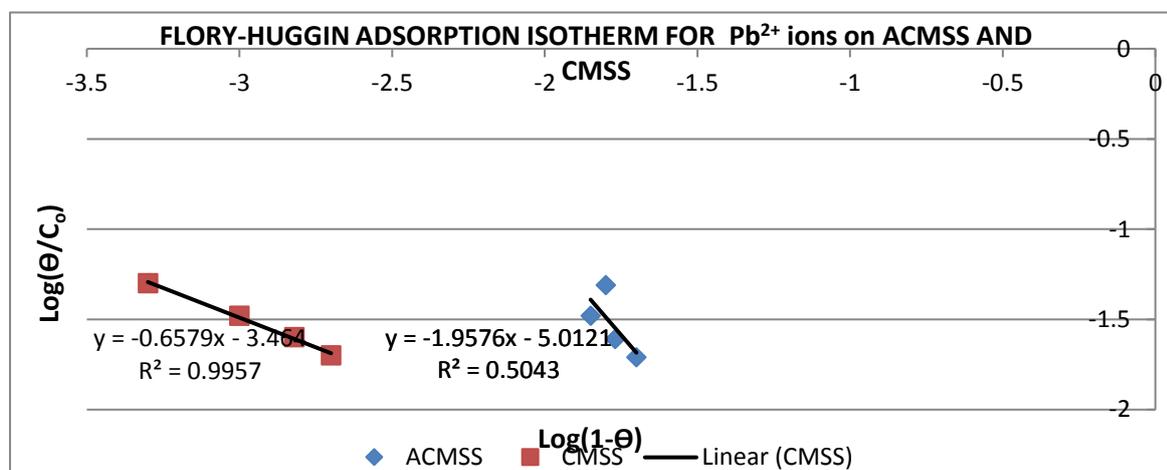


Fig. 7: Flory-Huggin Adsorption Isotherm for the sorption of Pb^{2+} ions on ACMSS and CMSS

The ACMSS had a stronger adsorption capacity and adsorption strength than CMSS judging from their values of K_F , n_F from the Freundlich adsorption isotherm model (Table 2). This is an indication that ACMSS form relatively stronger bonds between itself and the Pb^{2+} ions. The maximum adsorption value (q_m) from Dubinin-Radushkevick (DRK) adsorption isotherm model, revealed that the ACMSS adsorbed Pb^{2+} ions slightly more than the CMSS. The transferred Pb^{2+} ions on the CMSS surface is more spontaneous than that of ACMSS based on the fact that the average free energy of adsorption per molecule (β) for ACMSS is higher than that of CMSS (Table 2). The energy of adsorption (E) for CMSS was higher than that of ACMSS, an indication that the quantity of Pb^{2+} ions adsorbed by CMSS will be lower compared to that of ACMSS as reflected by K_F and q_m in Table 2. The process of adsorption of Pb^{2+} ions onto ACMSS and CMSS was a physical process this was a reflection of their values of energy of adsorption (Table 2).

Table 2: parameters of Adsorption isotherm models for adsorption of Pb²⁺ ions onto ACMSS and CMSS

Adsorption Isotherm Model	Parameters	Units	CMSS	ACMSS
Freundlich $\log q_e = \log k_f + (1/n_f)\log C_e$	R ²	-	0.94	1.00
	K _F	L/mg	9.44	20.42
	n _F	-	1.01	2.52
Dubinin-Radushkevick (DRK) $\ln q_e = \ln q_m - \beta \cdot \varepsilon^2$ $[\varepsilon = RT \ln(1+1/C_e)]$	R ²	-	0.98	0.99
	q _m	mg/g	10.87	11.00
	β	mol ² /J ²	-9.00x10 ⁻⁹	-1x10 ⁻⁷
	E	kJ/mol	7.45	2.24
Flory-Huggins $\text{Log}(\theta/C_0) = \text{Log} K_{FH} + n \text{Log}(1-\theta)$ $[\theta = (1- [C_e/C_0])]$	R ²	-	1.00	0.50
	K _{FH}	Lmol ⁻¹	3.52x10 ⁻⁴	9.73x10 ⁻⁶
	n _{FH}	-	0.66	1.92
	ΔG	KJ	+20.03	+29.19

The adsorption process of ACMSS and CMSS was non-spontaneous and supports endothermic nature by virtue of the fact that the standard change in the free energy (ΔG) is positive. The ACMSS adsorption of Pb²⁺ ions was more non-spontaneous compared to CMSS (Table 2). This could be attributed to the increased pore opening in ACMSS compared to CMSS (Fig. 2 and 3), the availability of more functional groups on ACMSS which are capable of adsorbing or complexing Pb²⁺ ions as shown on the FTIR chart (Fig. 4) and some process of chemisorption was suspected.

CONCLUSION

The adsorption process of Pb²⁺ ions on ACMSS and CMSS was physiosorption. ACMSS had a stronger adsorption capacity and adsorption strength than CMSS due to the relatively stronger bond between ACMSS and Pb²⁺ ions. The ACMSS and CMSS are good materials that can be effectively used as an adsorbent for the removal of Pb²⁺ ions from aqueous solution, however, the adsorption capacity of the ACMSS was preferable and good enough to be recommended for use in removing Pb²⁺ ion from Pb²⁺ ion contaminated water ahead of CMSS. This study has been able to device a means of solving the nuisance which mango seed constitute to the environment during and after its season. In other words, this is a means of converting waste to wealth and a means of treating Pb²⁺ ion contaminated waters.

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