Adsorption Dynamics of Agricultural Waste Activated Carbon in Water Quality Improvement

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Abstract — This study investigated the removal of Lead and Cadmium ions from aqueous solution using activated carbons from agricultural wastes. Activated carbons prepared by chemical activation using Phosphoric acid were characterized by Fourier Transform Infrared (FTIR), Scanning Electron Microscopy (SEM) and Brunauer-Emmett-Teller (BET) analysis. The influence of contact time, initial concentration and adsorbent dose which governed the efficiency of the process was ascertained through batch adsorption studies. Adsorption isotherms were determined by correlating with Langmuir and Freundlich isotherms and the kinetic studies were correlated with pseudo first order and pseudo second order equations. The results showed that the amount of Lead and Cadmium adsorbed decreased as the adsorbent dose increased while the adsorption capacity increased with increased in contact time and initial concentration. Activated carbons prepared from Coconut shell and palm kernel (shell and cake) competed favorably with the commercial activated carbon in percentage removal of the metal ions as all the activated carbons had over 90 % removal within 60 minutes when 1g of adsorbent was used. The equilibrium data fitted best into Freundlich isotherms for both metal ions. The rate of adsorption could be described by pseudo second order for all the adsorbents except Coconut shell activated carbon in the adsorption of Lead while intra-particle diffusion was the limiting step for Cadmium adsorption. Therefore, the agricultural by-products can be used as effective, low-cost, and environmentally friendly adsorbents for domestic water treatment in many parts of the world.

Key words — Activated carbon, Adsorption, Agricultural waste, Cadmium, Isotherm, Kinetics, Lead.

I. INTRODUCTION

Heavy metal pollution of water has become a threat to the environment and public health due to its toxicity, accumulation in food chain and presence in nature [1]. The conventional methods for heavy metal removal from water and wastewater include oxidation, reduction, precipitation, membrane filtration, ion exchange and adsorption [2]. Adsorption method has been found to be less expensive and useful in environmental application such as wastewater treatment, where it is used for purification, decolourization and the removal of toxic organics and heavy metal ions

Activated carbon is one of the most effective, versatile, and useful adsorbents for the removal of pollutants from polluted gas and liquid streams because of its large adsorption capacities, extremely high surface areas, well developed pore

structures, fast adsorption kinetics and good mechanical properties [3], [4]. Commercial activated carbon is a well-known adsorbent for the removal of heavy metals from water and wastewater, but the high cost of commercial activated carbon has limited its use as adsorbents in developing countries. Over the years, there has been a growing need to produce activated carbon from low cost, easily available and eco-friendly agricultural waste for the adsorption of heavy metals from water sources. The conversion of agricultural wastes to value added product such as activated carbon will be an excellent method to solve environmental problem as well as generate income for local communities.

Activated carbon can be manufactured from virtually all carbonaceous materials. However agricultural wastes offer the most available and cheapest of all the known raw materials [5]. They can be prepared from a large number of raw materials; especially agro-industrial by-products like palm kernel shells, Bamboo sticks, fruit seed shells, coconut shell. A lot of research has been done on activated carbon to improve the applicability of activated carbon as a cheap, effective, and eco-friendly adsorbent.

This study, therefore, compares the adsorption capacities of commercial activated carbon with activated carbons produced from low cost and commonly available agricultural bio-waste for the treatment of domestic water, contaminated with heavy metals in Eastern Obolo, Niger Delta, Nigeria.

II. EXPERIMENTAL

A. Raw Material Preparation

Three activated carbons were prepared from coconut shell (CSAC), palm kernel shell (PKSAC) and palm kernel cake (PKCAC). The agricultural wastes were sourced locally from oil palm processing mills and markets in Eastern Obolo. The raw materials were reduced to small sizes with locally fabricated palm kernel cracking machine. The samples were washed with hot water and sun dried for four days. The palm kernel cake was then soaked in acetone for 12 hours and then dried in an oven at 150 °C for 4 hours.

The coconut shell and palm kernel shell were carbonized in a Carbolite muffle furnace at 700 °C for 1 hour, while the palm kernel cake was carbonized at 500 °C also for 1 hour. The carbonized coconut and palm kernel wastes were soaked in 30% H₃PO₄ for 48 hours before further carbonization of coconut and palm kernel shell at 800 °C, and palm kernel cake

Submitted on October 01, 2021.

Published on October **, 2021.

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at 600 °C for 30 minutes. The activated samples were then cooled at room temperature, washed severally with distilled water to pH of 5-7, and dried in the oven at 110 °C for 4 hours. The carbonized waste materials were then grinded into powder with heavy duty blinder. The final samples were sieved to particles size 60 mesh (0.250 mm) $\cong$ 250 micron and kept in an airtight polyethylene bags for use in the adsorption experiment. A commercially prepared activated charcoal powder (CAC) from CDH, New Delhi, India was used for comparison.

B. Stock Solution Preparation

A stock solution of Cadmium (II) concentration 1000 mg/l was prepared by dissolving 363.39 mg of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in 1000 ml distilled water. While Lead (II) concentration was prepared by dissolving 624.98 mg of $\text{Pb}(\text{NO}_3)_2$ in 1000mls distilled water. The desired concentrations for the experiment were prepared by further dilution of the stock with distilled water. All Chemicals used were of analytical grades.

C. Batch Adaptation Equilibrium and Kinetic Studies

Batch adsorption experiment was used to investigate the adsorption of Lead (Pb) and Cadmium (Cd) from aqueous solution. Wastewater samples were simulated in the laboratory by dissolving $\text{Pb}(\text{NO}_3)_2$ and $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ salts in 1000 ml of distilled water to form the stock solution of Lead and Cadmium (1 mg/ml), respectively, which were then diluted to obtain the desired initial concentration for the adsorption experiments. The optimum conditions for the adsorption of Pb and Cd were investigated at room temperature (28 ± 1 °C). In each adsorption experiment, 50 mL of metal ion solution with a known concentration was added to 1 g of adsorbent in a 250 mL glass-stoppered flask, and the mixture was stirred on a mechanical shaker for 150 minutes at 150 rpm. The samples were withdrawn during stirring at preset time intervals, and the solutions were filtered with Whatman filter paper, and the filtrates were then separately analyzed for residual concentrations of metal ions by Atomic Absorption Spectrometer (AAS). For each batch run, the amount of metal ions adsorbed per unit mass of activated carbon at equilibrium q_e (mg/g), at time t , q_t (mg/g) and the percentage (%) removal of metal ions was determined using Equations (1, 2 and 3), respectively:

$$q_e = \frac{(C_o - C_e) \times V}{M} \quad (1)$$

$$q_t = \frac{(C_o - C_t) \times V}{M} \quad (2)$$

$$\% \text{ removal of crude oil} = \frac{(C_o - C_e) \times 100}{C_o} \quad (3)$$

where

C_o = Initial concentration of solution (mg/L);

C_e = Equilibrium concentration (mg/L);

C_t = concentration of solution at time, t (mg/L);

V = Volume of the solution (L);

M = Mass of adsorbent used (g).

The initial concentration of the simulated wastewater was varied along with the contact time and the adsorbent mass. The equilibrium data obtained were used for the kinetic studies and also fitted into Langmuir and Freundlich isotherm models.

The isotherm equations were explained using the goodness of fit, R^2 and other error functions. According to the (R^2) value, the higher the R^2 value (closer to unity) the better the model for depicting the isotherm parameters [6].

Similarly, the kinetic data were also fitted into pseudo-first order, pseudo-second order and intra-particle. In all adsorption studies, R^2 was used to test goodness of fit.

III. RESULTS AND DISCUSSION

A. Characterization of Adsorbent

Physico-chemical characteristics and potential uses of adsorbents are greatly influenced by the biomass feedstock, precursor pretreatments, carbonization method and activating condition [7]. The morphological structure of the activated carbons was analyzed with the aid of Scanning Electron Microscopy (SEM) and the images of the different activated carbons used for the experiment are presented in Fig. 1 a, b, c, and d. The surface structure developed pores and some cavitation in the process of carbonization and activation. SEM images of the activated Carbons revealed rough, porous surfaces with cavitation. The surfaces of the commercial activated Carbon showed more cavitation and cracks than others. CSAC had some of the pores partially blocked. Prominent bright silver patches were seen on the surface of PKCAC suggesting the presence of iron oxide which is in line with the study reported by [8]. The high porosity of PKCAC is known to increase adsorption capacity [5]. The image of activated Carbon prepared from Palm Kernel Shell (PKSAC), showed smooth surface with scanty tiny pores.

The elemental composition of the activated carbons determined by Energy Dispersive X-ray (EDX) is shown in Table I and revealed significant percentage of eight elements: Carbon (C), Oxygen (O), Phosphorous (P), Aluminum (Al), Sodium (Na), Potassium (K), Silicon (Si) and Iron (Fe). The activated carbons were composed of carbon and oxygen predominantly. Energy Dispersive X-ray analysis for elemental composition of the carbons as shown in Table 1 revealed CSAC with carbon content of 69.32%, as the highest followed by PKCAC 56.24% and PKSAC 56.21%. The least in carbon content is CAC with 18.39%. The high carbon content of activated carbons prepared from Coconut shell and Palm kernel shell and cake in this study was similar to the findings in the study by [7]. This indicates that PKSAC, PKCAC, and CSAC fit into active carbons [7]. Therefore, the prepared activated carbons in this study are preferred to the commercial carbon as a result of the higher carbon content. [7], stated that Oxygen content from the elemental analysis is also an important aspect, because it can form oxygen functional groups which aid adsorption process. Oxygen content of the activated carbons in Table I is as follows: CSAC 15.01%, PKSAC 35.51%, PKCAC 21.91% and CAC 18.39%. The high oxygen content of the adsorbents may have contributed significantly to the high percentage removal of toxic metal ions noticed in the study.

Fig. 1. Scanning Electron microscopy (SEM) images of (a) Commercial Activated Carbon (CAC), (b) Coconut Shell Activated Carbon (CSAC), (c) Palm Kernel Cake Activated Carbon (PKCAC) and (d) Palm Kernel Shell Activated Carbon (PKSAC).

Brunauer-Emmett-Teller (BET) analysis was carried out to determine the surface areas, pore volumes and pore sizes of the different activated Carbons. The result shown in Table II, gave the surface areas as follows: CSAC 826.488 m²/g, CAC 626.988 m²/g, PKSAC 602.074 m²/g and PKCAC 557.912 m²/g. Pore size and pore volume are also shown in Table II. The BET surface area of the activated carbons shown in Table II is in the order: CSAC > CAC > PKSAC > PKCAC with good surface areas for adsorption. Large surface areas show possibility of high adsorption of organic compounds [5]. All the activated carbons demonstrated mesopore size except CSAC which showed a micropore size of less than 2 nm according to IUPAC classification. The high surface areas observed in the study was also reported in a study by [7], which he attributed to highly developed pore network within the carbon as a result of the ability of the activating agent (Phosphoric acid) to penetrate deep into the structure of the carbon causing tiny pores to develop.

Spectra of Fourier Transform Infrared (FTIR) for the different activated Carbons shown in Fig. 2 a, b, c and d established the presence of different peaks corresponding to different functional groups along the wavelength 4000-640 cm⁻¹. All the activated carbons except CSAC showed strong peaks between 3000-3700 cm⁻¹ which suggest the presence of O-H stretching vibrations of water moieties [5], [8]. PKCAC and CSAC have peaks between 2600-2900 cm⁻¹ which correspond to C-H stretching vibrations from methyl group [9], [7]. PKSAC and CAC did not demonstrate the presence of this functional group. The C=O stretching of

Carboxylic acid seen between 2000-2500 cm⁻¹ [5] were found in all the carbons, also found in all the activated carbons were the C-O and C=O stretching corresponding to alcohol and carbonyl group between 1000-1600 cm⁻¹ [5]. These different functional groups, particularly oxygen containing functional groups had been known to enhance adsorption capacity of activated carbon through heavy metal binding on activated carbon surfaces [7], [10].

Fig. 2. (a). Spectrum of Commercial Activated Carbon (CAC).

Fig. 2. (b). Spectrum of Coconut Shell Activated Carbon (CSAC).

Fig. 2 (c). Spectrum of Palm Kernel Cake Activated Carbon (PKCAC).

Fig. 2 (d). Spectrum of Palm Kernel Shell Activated Carbon (PKSAC).

TABLE I: CHEMICAL COMPOSITION OF THE ACTIVATED CARBONS USING EDX ANALYSIS

Sample ID	C (%)	O (%)	P (%)	Al (%)	Na (%)	K (%)	Si (%)	Fe (%)
CSAC	69.32	15.01	7.85	2.09	2.29	0.67	0.67	0.00
PKSAC	56.21	35.51	1.62	1.50	0.87	0.00	1.39	0.00
PKCAC	56.24	21.91	10.44	1.79	1.00	1.01	1.44	1.08
CAC	18.39	32.94	0.89	6.58	9.80	0.47	15.15	2.67

TABLE II: THE SURFACE AREA AND PORE STRUCTURE CHARACTERIZATION OF THE PREPARED ACTIVATED CARBONS

Sample ID	Langmuir (m ² /g)	Multi-Point BET (m ² /g)	Pore Volume (cc/g)	Pore Size (nm)
CSAC	0.000	826.488	0.724	1.520
PKSAC	3259.799	602.074	0.549	2.920
PKCAC	2361.649	557.912	0.506	2.880
CAC	3229.914	626.958	0.571	2.920

B. Effect of Contact Time

The effect of contact time on the adsorption of metal ions was investigated and the result are as shown in Fig. 3 a and 3 b. Increase in contact time resulted in increase in percentage removal of Lead from solution until equilibrium was reached. All the adsorbents had over 93% removal of Lead within contact time of 15mins to 150 min. Equilibrium time was attained as follows: CSAC at 135min., PKSAC at 105min, PKCAC at 120 min and CAC at 105min. An initial rapid percentage removal of Lead was observed with CSAC. All the adsorbents used removed 99% of Lead from solution except CAC that removed 96.7% of lead within 60 minutes.

Similarly, percentage removal of Cadmium (Cd) increased steadily with the contact time for all the adsorbents until equilibrium was reached. From the results in Fig. 3 a and b, removal of Pb and Cd from the solution increased with contact time until the attainment of equilibrium which is in line with study by [1]. The finding was attributed to increase in Kinetic energy of the metal ions and decrease in boundary layer resistance due to mass transfer in the bulk solution. This observation was also corroborated by [10]. The increase in surface area of the adsorbent and the availability of active sites are believed to be responsible for the rapid adsorption of metal ions at the beginning stage of the reaction [8].

(a)

(b)

Fig. 3. The effect of contact time on the % removal of (a) Lead (Pb) and (b) Cadmium (Cd).

C. Effect of Adsorbent Dose on Percentage Removal of Pb and Cd

The effect of increase in doses of the different adsorbents from 1.0–3.0 g only resulted in marginal increase in percentage removal of both Pb and Cd with activated carbon produced from Coconut shell (CSAC) removing more than 99.8% as shown in Fig. 4 a and 4 b. The results in Fig. 4 a and b showing initial increase in percentage removable of both Cd and Pb with increase in adsorbent dose was in agreement with the study by [10] and was attributed to the increase in the number of adsorption site as the mass of adsorbent increases. [1], however noticed a decrease in the amount of metal ions adsorbed per unit mass of the adsorbent as the mass of adsorbent doses increased. They attributed the phenomenon to adsorption sites remaining unsaturated during adsorption.

(a)

Fig. 4. The effect of adsorbent dosage on the % removal of (a) Lead (Pb) and (b) Cadmium (Cd).

D. Effect of initial Adsorbate Concentration

The adsorption experiment was conducted to test the effect of initial concentration of the different adsorbates on the percentage removal of metal ions. There was an initial increase in percentage removal of Pb with increase in initial concentration of adsorbate to a climax before a steady decline in percentage removal except for PKCAC which showed no difference. The maximum efficiency of Lead removal for each of the adsorbents was reached at initial concentration of 6.25 mg/l for PKSAC and PKCAC, and 9.37 mg/l for CSAC and CAC. Cadmium (Cd) showed a steady increase in percentage removal with increase in initial adsorbate concentration except for Cd removal on coconut shell activated carbon (CSAC) which showed a similar pattern as observed with Lead (Pb) adsorption in Fig. 5 a and 5 b. CSAC performed better with Cd removal than the others. The removal of Cd from solution by adsorption unto the different adsorbents presented in Fig. 5 b showed an initial rapid increase in adsorption efficiency with increase in initial concentration of adsorbate in line with the report of [10] who studied the removal of heavy metals from solution using activated carbon prepared from seed shell and postulated that at lower concentration, the number of metal ions is low when compared to the available adsorbent active sites, therefore adsorption is more apparent. Thus, when equilibrium between the absorbed and the remaining ion in solution is established the rate of adsorption decreases. [1] also observed an increase in percentage removal with increase in ion concentration.

Fig. 5. The effect of adsorbate dosage on the % removal of (a) Lead (Pb) and (b) Cadmium (Cd).

E. Kinetic Studies

Several kinetic models have been applied to examine the controlling mechanism of metal adsorption from aqueous solution. This study applied pseudo-first-order, pseudo-second-order and intra-particle diffusion mechanism.

The different kinetic models for the adsorption of Pb and Cd onto the different adsorbents used in this experiment is compared using the goodness of fit (R^2) values as shown in Tables III A and III B. The adsorption of Pb unto CSAC followed Pseudo-first-order reaction with $R^2 = 0.999$ while the adsorption kinetic of Pb unto PKSAC and PKCAC followed pseudo-second-order kinetic with R^2 values of 0.987 and 0.972, respectively. Adsorption of Pb onto CAC followed an intra-particle diffusion kinetic with R^2 value of 0.816. The adsorption of Cd onto the different adsorbents used in this experiment as shown on Table III Bb fitted better with intra-particle diffusion kinetic than pseudo-second-order kinetic.

TABLE III A: ADSORPTION KINETIC MODEL CONSTANTS FOR THE REMOVAL OF LEAD (Pb)

Adsorbents	$q_{e,exp}$ (mg/g)	Pseudo-first order			Pseudo-second order		
		K_f (g/mg.min)	$q_{e,cal}$ (mg/g)	R^2	K_s (g/mg.min)	$q_{e,cal}$ (mg/g)	R^2
CSAC	0.155925	0.186139	0.155822	0.998776	6.311069357	0.1578150	0.856
PKSAC	0.155925	0.338535	0.155766	0.818312	50.37180073	0.1560913	0.987
PKCAC	0.15595	0.352876	0.155832	0.883904	68.50599128	0.1560493	0.972
CAC	0.15575	0.266836	0.152454	0.543857	11.84909063	0.1539730	0.637
Adsorbents	$q_{e,exp}$ (mg/g)	Intra-particle Diffusion					R^2
		K_{ip} (mg/g.min ^{1/2})	C (mg/g)	$q_{e,cal}$ (mg/g)			
CSAC	0.155925	0.000723	0.148534	0.154825	0.637809		
PKSAC	0.155925	0.000145	0.154501	0.155644	0.851408		
PKCAC	0.15595	0.0000941	0.154963	0.155744	0.806983		
CAC	0.15575	0.00087	0.145232	0.1521	0.816526		

TABLE III B: ADSORPTION KINETIC MODEL CONSTANTS FOR THE REMOVAL OF CADMIUM (Cd)

Adsorbent	$q_{e,exp}$ (mg/g)	Pseudo-first order			Pseudo-second order		
		K_f (g/mg.min)	$q_{e,cal}$ (mg/g)	R^2	K_s (g/mg.min)	$q_{e,cal}$ (mg/g)	R^2
CSAC	0.0907	0.187827	0.0877993	0.56878	6.564927	0.090056	0.716
PKSAC	0.09075	0.2374288	0.087562	0.53569	12.56569	0.088988	0.619
PKCAC	0.0908	0.2342341	0.0880262	0.53393	11.65175	0.089466	0.624
CAC	0.0906	0.2244527	0.0874525	0.55262	11.06641	0.089036	0.656

Adsorbent	$q_{e,exp}$ (mg/g)	Intra-particle Diffusion			
		K_{ip} (mg/g.min ^{1/2})	C (mg/g)	$q_{e,cal}$ (mg/g)	R^2
CSAC	0.0907	0.001105	0.077632	0.087248	0.921587
PKSAC	0.09075	0.000816	0.080803	0.087244	0.785414
PKCAC	0.0908	0.000802	0.081067	0.087728	0.814781
CAC	0.0906	0.000867	0.080222	0.087064	0.834752

F. Adsorption Isotherm

There are several isotherm models available for analyzing experimental adsorption equilibrium parameters, however the Langmuir and Freundlich models are commonly used. Tables IV A and IV B show the model parameters and the statistical fits of the adsorption data to Langmuir and Freundlich models. The coefficient of determination was calculated by fitting the experimental equilibrium data for Pb and Cd adsorption onto the different adsorbent performances using the two models. The results on Table IV A shows that, the adsorption of Pb onto CSAC and PKSAC fits well with the Freundlich model while the adsorption of Pb onto PKCAC and CAC fit with both Langmuir and Freundlich models. The result on Table IV B for the adsorption of Cd onto the different adsorbents show that the Freundlich model is a good fit to the experimental

adsorption data. The Langmuir isotherm model assumes a finite number of active sites which are homogeneously distributed over the surface of the adsorbent [11]. The active sites have the same affinity for adsorption of a mono molecular layer and there is no interaction between the adsorbed molecules [12]. This is physical adsorption due to weak Van der Waal forces.

The Freundlich isotherm model applies to adsorption on heterogeneous surface, and it is a multilayer adsorption [13].

From Tables IV A, the finding of adsorption of Pb onto PKCAC and CAC fitting well with both Langmuir and Freundlich models corroborates the finding of [10] for the adsorption of heavy metal from aqueous solution onto activated carbon adsorbent.

TABLE IV A: ADSORPTION ISOTHERM CONSTANT FOR THE REMOVAL OF LEAD (Pb)

Adsorbent	Langmuir			Freundlich		
	q_m (mg/g)	K_L (L/mg)	R^2	K_f (mg/g)	N	R^2
CSAC	1.259172	12.122	0.837	1.095641	1.44044	0.955736
PKSAC	0.676528	38.219	0.869	0.824011	3.52309	0.948091
PKCAC	23.48114	0.4099	0.986	9.053736	1.01271	0.987868
CAC	2.248968	1.0127	0.952	1.31664	1.22748	0.950246

TABLE IV B: ADSORPTION KINETIC MODEL CONSTANTS FOR THE REMOVAL OF CADMIUM (Cd)

Adsorbent	Langmuir			Freundlich		
	q_m (mg/g)	K_L (L/mg)	R^2	K_f (mg/g)	N	R^2
CSAC	0.322467	187.86	0.525	4.8007	1.2534	0.79295
PKSAC	135.8941	0.0298	0.517	1.9712	0.0351	0.924581
PKCAC	305.4831	0.0134	0.630	6.04 03	0.05797	0.864445
CAC	348.9372	0.0138	0.513	1.32 42	6	0.945523

G. Statistical Analysis of Adsorption Properties of the Bio-adsorbents

The result of the statistical analysis of differences in adsorption performance of the different bio-adsorbents using Kruskal Wallis are presented on Tables V and VI for Pb and Cd, respectively. Kruskal Wallis test is a non-parametric procedure that can be used to compare more than two populations. It identifies by ranks if three or more independent samples were selected from populations having the same distribution.

1) Lead (Pb) Adsorption

Result in Table V a reveals that there is no significant difference in the amount of Pb adsorbed for the different types of adsorbents used ($P > 0.05$), contact time ($P > 0.05$) while initial adsorbate concentration ($P < 0.05$) and adsorbent mass

($P < 0.01$) gave significant results with optimal Pb adsorption occurring at initial concentration of 15.62 mg/l and adsorbent mass of 1 g. The percentage of Pb removed differ significantly between the three types of adsorbents ($P < 0.01$) at the initial concentration ($P < 0.01$) and contact time ($P < 0.01$) while adsorbent mass gave insignificant result ($P > 0.05$). Result indicates that the highest percentage Pb removal was achieved when PKCAC was used (in preference to the other adsorbents) while in terms of initial concentration and contact time, the optimal result was obtained at 3.12 mg/l initial concentration and 135 minutes contact time.

2) Cadmium (Cd) Adsorption

Result in Table VI shows no significant difference in the amount of Cd adsorbed when the different types of the adsorbents were used ($P = 0.985$) and contact time ($P > 0.05$)

while significant results were obtained at the initial adsorbate concentration ($P < 0.01$) and adsorbent mass ($P < 0.01$) with initial concentration of 9.09 mg/l and adsorbent mass of 1g giving the highest amount of Cd adsorbed. There was no significant difference in % of Cd removed due to the different types of adsorbents ($P > 0.05$) and adsorbent mass ($P > 0.05$) whereas significant difference in % of Cd removed were obtained in relation to initial adsorbate concentration ($P < 0.05$) and contact time ($P < 0.01$). Result reveals that initial concentration of 9.09 mg/l and contact time of 135.00 minutes gave the highest % of Cd removed.

TABLE V: KRUSKAL WALLIS RESULT OF DIFFERENCES IN THE AMOUNT OF Pb ADSORBED AND ADSORPTION EFFICIENCY BASED ON ADSORBENT TYPE, INITIAL CONCENTRATION, ADSORBENT MASS AND CONTACT TIME

Variables	Amount of Pb adsorbed			% of Pb removed		
Types of adsorbent	Mean rank	Kruskal-Wallis χ^2	P-value	Mean rank	Kruskal-Wallis χ^2	P-value
CSAC	39.95	2.615	0.455	45.40	18.729	0.000**
PKSAC	39.47			39.36		
PKCAC	41.32			46.68		
CAC	30.86			19.25		
Initial conc.						
3.12	30.00	37.957	0.0000**	42.61	13.541	0.009**
6.25	61.50			29.25		
9.37	65.50			23.75		
12.50	69.50			16.25		
15.62	73.50			14.75		
Adsorbent mass						
1	46.00	37.588	0.0000**	37.53	0.521	0.971
1.5	10.67			42.08		
2.0	10.50			38.50		
2.50	6.50			41.50		
3.0	2.00			31.50		
Contact time						
15.00	22.88	8.235	0.511	14.38	29.398	0.0010**
30.00	30.25			35.00		
45.00	33.00			38.00		
60.00	36.24			31.40		
75.00	40.50			47.50		
90.00	42.75			50.50		
105.00	50.00			63.13		
120.00	52.13			65.63		
135.00	57.00			71.25		
150.00	55.50			69.50		

*Significant at 5% ($p < 0.05$), **significant at 1% ($p < 0.01$).

H. Adsorption Capacity Model

Three parameters were used to develop a mathematical model that relate Adsorption Capacity (AC) to contact time (t), adsorbate concentration (Co) and adsorbent mass (M) for the adsorption of Pb and Cd onto the different adsorbents (Equation (4)). The developed adsorption coefficients and exponential constants for the different adsorbents are summarized on Tables VII and VIII for Pb and Cd, respectively.

$$AC = \alpha_0 \left(\frac{t^{\alpha_1} \times C^{\alpha_2}}{M^{\alpha_3}} \right) \quad (4)$$

TABLE VI: KRUSKAL WALLIS RESULT OF DIFFERENCES IN THE AMOUNT OF Cd ADSORBED AND ADSORPTION EFFICIENCY BASED ON TYPE, INITIAL CONCENTRATION, AND ADSORBENT MASS AND CONTACT TIME

Variables	Amount of Cd adsorbed			% of Cd removed		
Types of adsorbent	Mean rank	Kruskal-Wallis χ^2	P-value	Mean rank	Kruskal-Wallis χ^2	P-value
CSAC	38.55	0.150	0.985	45.00	3.250	0.355
PKSAC	37.17			32.86		
PKCAC	39.26			37.55		
CAC	36.89			35.83		
Initial conc.						
1.82	30.00	37.942	0.0000**	33.64	11.478	0.022*
3.63	61.50			49.25		
5.45	65.50			52.25		
7.27	69.50			56.25		
9.09	73.50			58.50		
Adsorbent mass						
1.00	46.00	37.942	0.0000**	38.59	0.329	0.988
1.50	14.50			33.50		
2.00	10.50			34.75		
2.50	6.50			36.38		
3.00	2.50			38.63		
Contact time						
15.00	21.50	11.772	0.226	5.50	51.158	0.0000**
30.00	23.00			7.00		
45.00	25.50			9.50		
60.00	37.93			40.34		
75.00	34.25			18.25		
90.00	42.50			36.50		
105.00	52.38			67.88		
120.00	54.25			70.25		
135.00	56.50			72.50		
150.00	54.50			70.50		

*Significant at 5% ($p < 0.05$), **significant at 1% ($p < 0.01$).

Result shown in Table VII reveals that for all the adsorbent considered, more than 99.0% of the variation in adsorption capacity was accounted for by initial concentration, contact time and adsorbent mass. The adsorption of Pb onto the different adsorbents (CAC, CSAC and PKCAC), had ($P < 0.05$) which means that, as contact time and initial concentration increase significantly, there is a corresponding significant increase in adsorption of Pb while as the adsorbent mass increases significantly, the adsorption capacity decreases significantly except for PKSAC where $P > 0.05$ for contact time. This relationship between adsorption capacity and contact time, initial concentration and adsorbent mass is supported by [12], [1]. Results presented in Table VIII reveal that in all the adsorbents considered, more than 99.0% of the variation in adsorption capacity of the adsorbents for Cd adsorption was accounted for by initial concentration, contact time and adsorbent mass. The results show that; contact time, initial concentration and adsorbent mass all have significant impact on the adsorption capacity of CAC, CSAC, PKCAC and PKSAC for Pb adsorption ($P < 0.05$). This result implies that as the contact time and initial concentration increase significantly, there is a corresponding significant increase in adsorption capacity for Cd while as the adsorbent mass increases significantly, the adsorption capacity decreases significantly ($P < 0.05$) for the four types of adsorbents.

TABLE VII: SUMMARY OF THE ESTIMATES OF THE AC MODELS FOR Pb FOR THE DIFFERENT TYPES OF ADSORBENT

Types of adsorbent	Parameters	Estimates	Standard error	t-statistic	p-values	R ²	RMSE
CAC	Constant α_0	0.045614	0.001041	43.80963	0.0000**	0.999947	0.001362
	Contact time α_1	0.018727	0.005492	3.409990	0.0042**		
	Initial conc. α_2	0.994160	0.002248	442.3355	0.0000**		
	Adsorbent mass α_3	0.980693	0.015170	64.64747	0.0000**		
CSAC	Constant α_0	0.046379	0.001177	39.39801	0.0000**	0.999904	0.001740
	Contact time α_1	0.020258	0.005755	3.519945	0.0028**		
	Initial conc. α_2	0.983444	0.002671	368.1463	0.0000**		
	Adsorbent mass α_3	0.985489	0.018902	52.13683	0.0000**		
PKCAC	Constant α_0	0.049469	0.000193	255.8818	0.0000**	0.999998	0.000257
	Contact time α_1	0.002423	0.000916	2.646266	0.0183*		
	Initial conc. α_2	0.998240	0.000399	2499.465	0.0000**		
	Adsorbent mass α_3	1.004538	0.002837	354.1291	0.0000**		
PKSAC	Constant α_0	0.050868	0.001669	30.46942	0.0000**	0.999881	0.002033
	Contact time α_1	0.004089	0.007919	0.516362	0.6137		
	Initial conc. α_2	0.973532	0.003304	294.6947	0.0000**		
	Adsorbent mass α_3	1.013823	0.022661	44.73961	0.0000**		

*Significant at 1% ($p < 0.01$), **Significant at 1% ($p < 0.01$).

TABLE VIII: SUMMARY OF THE ESTIMATES OF THE AC MODELS FOR Cd FOR THE DIFFERENT TYPES OF ADSORBENT

Types of adsorbent	Parameters	Estimates	Standard error	t-statistic	p-values	R ²	RMSE
CAC	Constant α_0	0.041503	0.001271	32.66236	0.0000**	0.999914	0.001045
	Contact time α_1	0.033050	0.007409	4.460902	0.0005**		
	Initial conc. α_2	1.020699	0.002975	343.0964	0.0000**		
	Adsorbent mass α_3	0.996402	0.020534	48.52354	0.0000**		
CSAC	Constant α_0	0.040024	0.001650	24.26038	0.0000**	0.999774	0.001256
	Contact time α_1	0.042286	0.009503	4.449577	0.0004**		
	Initial conc. α_2	1.021837	0.004314	236.8889	0.0000**		
	Adsorbent mass α_3	0.967301	0.030502	31.71238	0.0000**		
PKCAC	Constant α_0	0.041997	0.001117	37.59306	0.0000**	0.999855	0.000970
	Contact time α_1	0.030808	0.006256	4.924813	0.0002**		
	Initial conc. α_2	1.019429	0.003417	298.3013	0.0000**		
	Adsorbent mass α_3	1.007828	0.019189	52.52115	0.0000**		
PKSAC	Constant α_0	0.041950	0.001226	34.20336	0.0000**	0.999921	0.001000
	Contact time α_1	0.030651	0.007078	4.330611	0.0007**		
	Initial conc. α_2	1.019353	0.002848	357.8927	0.0000**		
	Adsorbent mass α_3	1.008744	0.019838	50.84968	0.0000**		

*Significant at 1% ($p < 0.01$), **Significant at 1% ($p < 0.01$).

IV. CONCLUSION

This study was undertaken to evaluate the adsorption of Lead and Cadmium on activated carbons from commonly available agricultural wastes. The prepared carbon from the by-products of coconut and palm kernel competed effectively with commercial activated Carbon for the adsorption of the metals and can be used for domestic water treatment. The adsorption of Pb and Cd on the activated carbons was found to be dependent on time, initial concentration of adsorbate and dose of adsorbent.

The removal efficiency of the different adsorbents was above 93% within 60 minutes for both metal ions. The kinetic data follow pseudo first order kinetic model for adsorption of Pb on CSAC, while pseudo second order for PKSAC and PKCAC. The intra-particle diffusion was the rate limiting step for Pb adsorption onto the commercial carbon. Cadmium adsorption on all the activated carbons used, followed the intra-particle diffusion kinetic.

The adsorption behavior of Pb and Cd was described by Langmuir and Freundlich isotherms, but the equilibrium data fitted best into the Freundlich equation for the adsorption of Cd on to all the activated carbons but the adsorption of Pb on CSAC and PKSAC fitted best into Freundlich isotherm, while adsorption onto PKCAC and CAC fitted both Langmuir and Freundlich isotherms well. There was no statistically significant difference in the amount of adsorbate adsorbed on to the activated carbons based on the types of adsorbents,

however, the removal efficiency was different for Pb adsorption.

This study showed that the prepared activated carbons from the locally available low-cost bio-wastes can effectively remove Pb and Cd from aqueous solution to avert expensive commercial adsorbents.

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