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Adsorption of Zinc on Cassava Peels Activated Carbon and Kaolin Clay: Kinetics, Thermodynamics and Optimization Studies

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ABSTRACT

Zinc in industrial, agricultural and domestic effluents gets into the human system and becomes toxic upon accumulation. The kinetics, thermodynamics and optimization of the process parameters for the adsorptions of zinc from zinc chloride (ZnCl2) simulated aqueous effluent using cassava peels activated carbon and kaolin clay were investigated. Proximate and oxide analyses carried out on the raw peels and the clay showed that the peels had 45% fixed carbon and the clay had more than 2% oxides of calcium, magnesium and iron in addition to alumina and silica. Whereas activated carbon was produced from the peels by carbonization at 700°C for 2hours in a muffle furnace, and subsequent treatment with phosphoric acid at 800°C for 2hours, the clay was not modified. The adsorption data generated at different levels of contact time were modeled and the pseudo-second-order kinetics model was adequate for the kinetics of the system at room temperature with regression coefficient (R2) of 0.998. The adsorption data also fitted into Langmuir, Freundlich and Temkin isotherms with a monolayer adsorption capacity of 4.8mg/g and 3.1mg/g for the activated carbon and clay respectively. The thermodynamic showed that the adsorption processes were endothermic and the magnitude of the standard enthalpy change showed that the adsorptions on the clay were more of physisorption while the adsorptions on the activated carbon were more of chemisorptions. Equally, the negative standard Gibb's free energy change showed that the processes were spontaneous. Optimization of the process parameters was carried out using the Box-Behnken design of Response Surface Methodology (RSM) and it was analyzed using Design Expert. Linear model was selected with R-squared, Adjusted R-squared and predicted R-squared values of 0.90, 0.89 and 0.88 respectively. The Analysis of Variance (ANOVA) of the model parameters showed that the effects of the five numeric factors, which are time, temperature, pH dosage and initial concentration, were statistically significant with p-values less than 0.01. It also showed that the effect of the one categorical factor, which is the type of adsorbent (clay or activated carbon), was statistically significant with the p-value less than 0.01. The numerical optimum solutions of the process parameters were obtained with theoretical percentage removal of 88% and 81% of zinc on cassava peels activated carbon and kaolin clay respectively.

Key Words: *Adsorption, Clay, Carbon, Kinetics, Thermodynamics, Optimization.*

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1. INTRODUCTION

Adequate water availability in terms of quantity and quality is essential to human life. Before the advent of industrial revolution, the importance of water from a quantity point of view was of more concern than the quality of water [1]. Civilization, in order to meet up with the needs of the ever-increasing human population triggered different unnatural activities around water bodies. These human activities meant to support agriculture, transportation, industrialization, and for drinking purpose created more concern on the quality of water. Specifically, discharge of toxic industrial wastes and untreated sanitary, dumping of industrial effluent, and runoff from agricultural fields can be the main sources of freshwater pollution [2]. The link between water and diseases has been long established and it became a global problem precisely in the mid nineteenth century [1].

The impurities accumulated in water by human activities may be in both suspended and dissolved form. All metals are soluble to some extent in water and the excessive amount of any metal may present health hazard. Those metals like lead, arsenic, barium, chromium, mercury and silver that are harmful in relatively small amounts are called toxic metals [3]. Zinc is a metal that is required especially in humans as a coenzyme, for wound healing, for DNA synthesis, and generally to maintain good health [4]. However, excess amount of zinc is harmful and toxic to human being [5]. Zinc dissolves in water through industrial, agricultural and domestic processes and when the water is discharged without any treatment, the zinc will directly or indirectly get into the human system and becomes a health hazard upon accumulation.

Adsorption process is said to be the most effective and widely used means of metal removal from waste water. This is basically due to less investment in terms of cost, simple and easy operation [6]. Adsorption involves the use of solid materials known as the adsorbents that have internal pores where the molecules to be removed will be attached. Recently, many waste biomasses, in and outside Nigeria, have been investigated as activated carbon adsorbents for metal and other pollutant removal from water. Nigerian bamboo was said to be effective in zinc removal [7].The use of activated carbon from bamboo, palm kernel and coco nut shells to remove benzene from effluent was investigated [8]. Cassava peel activated carbon was used for total waste water treatment [9]. The adsorption of copper with Columbian cassava activated carbon was carried out and it was stated that cassava peels activated with $ZnCl_2$ was effective in removal of Cu^{2+} in aqueous solution [10]. Over 14 million tonnes of cassava peels are produced as waste material in Nigeria [11]. Using cassava peels activated carbon to treat zinc-contaminated water could be of high economic importance owing to the abundance of the peels.

Kaolin is a soft white mineral that has a large array of uses [13]. Kaolin can be found abundantly in Nigeria where it is mainly used for porcelain production and has been investigated and found to be effective in the removal of toxic metals from waste water [14]. It was found to be effective in the adsorption of methylene blue [13], nitrate [15], hexavalent chromium [16], Congo Red [17] from aqueous solution. This report investigated and compared the zinc adsorptive strength of cassava peels activated carbon and raw kaolin clay. The kinetics, thermodynamics and the optimization of process parameters were deemed necessary for the purpose of process design for industrial and large-scale uses.

2. MATERIALS AND METHOD

2.1. Raw materials preparation

Cassava peels were obtained from Nsukka native home in Enugu State Nigeria. The peels were sun dried, ground to powder and sieved to obtained fine particle of uniform size of 250µm using electromagnetic sieve shaker (BA, 200N model). The kaolin clay was obtained from the Ceramics Department of PRODA in Enugu Nigeria. The clay was ground and sieved to get a uniform particle size used for the experiment. The clay was not treated any further before the adsorption experiment.

2.2. Proximate analysis of cassava peels

The proximate analysis parameters and the methods of analyses were according to the American Society for Testing and Materials (ASTMD 5142, 3174, 872 and 3175 for moisture, ash, volatile and fixed carbon respectively) [18]. The methods of the analysis are outlined below:

2.2.1. The moisture content

The moisture content of the original cassava peels was determined by weighing 1g of the sample using an electronic weighing balance (Model PA 213) in a Petri dish and placing the dish in an oven (DHG-9101-ISA) at 105°C for 1hour. After which the dish was allowed to cool in desiccators and weighed. Drying in the oven was repeated until a constant weight was obtained. Moisture content was calculated using the formula in (1)

$$\%\, moisture = \frac{w_2 - w_3}{w_2 - w_1} \times 100 \qquad (1)$$

Where

W_1=weight of empty crucible

W_2= weight of crucible +sample before heating

W_3=weight of crucible + sample after heating

2.2.2. The volatile matter content

The volatile matter content was obtained by heating the moisture free sample with a porcelain crucible in a muffle furnace (SX-5-12 model) at 900°C for 10min. Heating in the absence of air at high temperature removes the volatile matter only. The volatile matter was calculated using the formula in (2)

$$\%\ volatile\ matter = \frac{w_5 - w_4}{w_2 - w_1} \times 100 \qquad (2)$$

Where

W_5= weight of porcelain crucible + moisture- free sample before heating

W_4=weight of porcelain crucible + sample after heating

W_2-W_1= original weight of sample

2.2.3. The fixed carbon and ash contents

The fixed carbon content of the sample was obtained by completely combusting the volatile-free sample with platinum crucible in a Bunsen burner. The residue left was the ash content while the fixed carbon was determined by difference using (3). The percentage ash content was calculated using (4).

$$\%\ fixed\ carbon = \frac{w_7 - w_8}{w_2 - w_1} \times 100 \qquad (3)$$

$$\%\ ash = \frac{w_8 - w_6}{w_2 - w_1} \qquad (4)$$

Where

W_7= weight of platinum crucible + volatile free sample before heating

W_8= weight of platinum crucible + sample after heating

W_6=weight of empty platinum crucible

W_2-W_1= original weight of sample

2.3. The Oxide analysis of the kaolin clay

Following the method described by reference [19], the oxide analysis of the clay was carried out. The clay was digested using a combination of hydrofluoric acid (HF) and aqua ragia as follows: 0.5g of the clay was weighed into a Teflon crucible. 5mL of aqua ragia was added followed by 15mL of HF. The crucible was placed inside the oven at 120°C and the clay was allowed to digest until a clear mixture was obtained. The digested clay solution was diluted to 100mL with distilled water and filtered using filter paper. The concentration of each of the filtrates determined using Atomic Absorption Spectrophotometer (AAS) (Bulk Scientific 210VGP). Concentration in ppm was converted to percentage using the formula in (5).

$$conc\ (\%) = \frac{Conc\ (ppm)}{50} \qquad (5)$$

2.4. Adsorbents preparation

The cassava peels powder was carbonized in a muffle furnace (SX-5-12model) at 700°C for two hours. After the carbonization the powder was chemically activated with phosphoric acid. The powder was soaked in one molar solution of phosphoric acid and dried at 100°C for 2hours, after which the impregnated powder was carbonized again at 800°C for 2hours. The carbon was washed severally with distilled water until neutral pH was obtained. The carbon was collected and dried in oven at 120°C for 2 hours [20]. The dried adsorbent was ground and kept in a bottle for use as an activated carbon.

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2.5. Adsorbate preparation

A synthetic effluent of Zinc was prepared using Zinc nitrate salt. To prepare a given concentration of the Zinc effluent, the molar mass of the salt was divided by the molar mass of Zinc; the result was multiplied by the gram equivalent of the needed concentration. 10ppm of the Zinc effluent was prepared by dissolving 0.3g of Zinc nitrate salt in 1liter volumetric flask and making the flask to the mark with distilled water.

2.6. The effect of time on the adsorption of zinc and the kinetics models

To investigate the effect of time on the adsorption of Zinc using the activated carbon and the clay, 0.2g of the carbon or clay was weighed into six different 250ml conical flasks, 20ml of 10ppm zinc effluent was added into each of the flask. The flaks were put in a mechanical shaker (model HY-4) and allowed to shake for 10, 20, 30, 40, 50, 60 minutes respectively. The solution was filtered into another set of conical flasks and the concentration of Zinc was measured using atomic absorption spectrophotometer (AAS) (Bulk Scientific 210VGP).

The kinetics model of the adsorption was investigated using the pseudo first and second order kinetic model shown in (6) and (7). Pseudo first order kinetics predicts the system where diffusion through a boundary precedes the adsorption [21].The pseudo second order model was derived on the assumption that the sorption capacity is proportional to the number of active sites occupied on the sorbent [22].

$$\text{First order kinetics equation: } \log(qe - qt) = logqe - \left(\frac{k_1 t}{2.303}\right) \tag{6}$$

$$\text{Second order kinetics equation: } \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{7}$$

Where

qe= adsorption capacity at equilibrium

qt= adsorption capacity at any time t

K_1 and K_2 are the pseudo first and second order constants respectively.

2.7. The effect of adsorbate concentration on the adsorption

Different concentration of the zinc effluents (10ppm, 20ppm, 30ppm, 40ppm) were prepared as described in section 2.5. 20mL of each of the concentration was added into different conical flasks. 0.2g of the adsorbents was also added into the flasks. The flasks were shaken for 60minutes. After which the solution was filtered into another set of conical flasks. The zinc concentration of the filtrates were determined using AAS. The percentage removal of zinc (%R) and the adsorption capacity (qt) were calculated using (8) and (9) below [21]:

$$\%R = \frac{C_o - C_e}{C_o} \times 100 \tag{8}$$

$$q_t = \frac{(C_o - C_e) \times V}{M} \tag{9}$$

Where

%R= percentage removal

q_t= adsorption capacity (ppm)

C_o=Initial concentration (ppm)

C_e=Equilibrium concentration (ppm)

V=Volume of effluent (L)

M=mass of adsorbent (g)

The adsorption was modeled using different adsorption isotherms as discussed below.

2.7.1. Langmuir adsorption isotherm:

This isotherm was based on different assumptions one of which is that dynamic equilibrium exists between adsorbed gaseous molecules and the free gaseous molecules [23].

$$A(g) + B(s) \xrightleftharpoons[\text{desorption}]{\text{Adsorption}} AB \qquad (10)$$

In (10), A(g) is unadsorbed gaseous molecule, B(s) is unoccupied adsorbent surface and AB is Adsorbed gaseous molecule.

Based on his theory, Langmuir derived the equation (11) which depicted a relationship between the number of active sites of the surface undergoing adsorption and pressure.

$$\theta = \frac{KP}{1+KP} \qquad (11)$$

Where θ the number of sites of the surface which are covered with gaseous molecule, P represents pressure and K is the equilibrium constant for distribution of adsorbate between the surface and the gas phase .The basic limitation of Langmuir adsorption equation is that it is valid at low pressure only. Relating the equation to ion adsorption in aqueous solution where P is analogous to Ce, and θ is analogous to qe/ql, gives (12) [24],[23],[25].

$$\frac{C_e}{q_e} = \frac{1}{q_l K_l} + \frac{C_e}{q_l} \qquad (12)$$

where $q_l = \text{monolayer adsoprtion capacity(mg/g)}$,

$K_l = \text{adsorption constant(Lit/mg)}$

2.7.2. Freundlich adsorption isotherm

In 1909, Freundlich gave an empirical expression representing the isothermal variation of adsorption of a quantity of gas adsorbed by unit mass of solid adsorbent with pressure. This (13) is known as Freundlich Adsorption Isotherm or Freundlich Adsorption equation or simply Freundlich Isotherm [23].

$$\frac{x}{m} = KP^{\frac{1}{n}} \qquad (13)$$

Where x is the mass of the gas adsorbed on mass m of the adsorbent at pressure p and k, n are constants whose values depend upon adsorbent and gas at particular temperature. Though Freundlich Isotherm correctly established the relationship of adsorption with pressure at lower values, it failed to predict value of adsorption at higher pressure. Freundlich isotherm is however, used at low pressure (or concentration) where Langmuir isotherm cannot be used [24].

Application of the equation to adsorption of metal ions in aqueous solution and making it linear yield the following (14) [24],[26]:

$$\log q_e = \log K_f + \left(\frac{1}{n}\right) \log C_e \qquad (14)$$

Where K_f (mg/g) and n are constants

qe=the equilibrium adsorption capacity (mg/g)

Ce=equilibrium concentration (mg/L)

2.7.3. Temkin isotherm

This isotherm contains a factor that explicitly taking into the account of adsorbent–adsorbate interactions [27]. By ignoring the extremely low and large value of concentrations, the model assumes that heat of adsorption (function of temperature) of all molecules in the layer would decrease linearly rather than logarithmic with coverage [28]. As implied in (15), its derivation is characterized by a uniform distribution of binding energies (up to some maximum binding energy)

$$q_e = B \ln A + B \ln C_e \tag{15}$$

where $\mathrm{B} = {}^{\mathrm{RT}}/_{\mathrm{b_T}}$

$\mathrm{T = temp(K);\ R = 8.314 J/mol.K.}$

b_T is the constant related to the heat of sorption and A is the equalization binding constant (L/mg)

2.8. The effect of temperature and the thermodynamics

The effect of temperature on the adsorption was determined by measuring 0.2g of the adsorbents into six different 250ml conical flasks and 20ml of 10 ppm zinc effluent was added into the flasks. The flasks were put inside water bath (DK600) with shaker set at 30, 40, 50, 60, 70, and 75°C respectively. The flasks were shaken for 60minutes after which it was filtered and the concentration of zinc was measured using the AAS. The standard free energy – $(\Delta G)°$, enthalpy change $(\Delta H)°$ and the entropy change $(\Delta S)°$ were determined to evaluate how spontaneous and feasible is the adsorption process. These thermodynamic parameters were calculated using (16-19) [29].

$$\Delta G° = -RTlnK_c \tag{16}$$

$$K_c = \frac{C_a}{C_e} \tag{17}$$

$$lnK_c = -\left(\frac{\Delta G°}{RT}\right) = -\frac{\Delta H°}{RT} + \frac{\Delta S°}{R} \tag{18}$$

$$C_a = C_0 - C_e; \tag{19}$$

Where

R=8.314J/mol.K;

C_e = Equilibrium concentration(mg/g)

C_o = Initial concentration(mg/g)

A plot of $\ln(K_c)$ against the inverse of temperature T(K) gives a straight line where the change in enthalpy (ΔH) and entropy (ΔS) are calculated from the slope and intercept respectively

2.9. The effect of pH on adsorption

To investigate the effect of pH on the adsorption, 0.2g of the adsorbents was measured into six different conical flasks containing 20ml of 10ppm of the Zinc effluent at different pH. The pH was adjusted using 1Molar concentration of HCl and NaOH. Measurement of the pH was by the use of a pH meter (Seven compact pH/ion S220). The flasks were put in a shaker for 60minutes after which the solution was filtered and the zinc concentration was measured using the AAS.

2.10. The effect of dosage on adsorption

The effect of dosage was investigated by measuring different grams of the adsorbents in different conical flasks containing 20ml of 10ppm Zinc effluent. The flasks were put in a shaker and allowed to shake for 60minutes. After which, the solution was filtered and the zinc concentration was measured using the AAS

3. RESULTS AND DISCUSSION

3.1. Proximate analysis result for cassava peels

The proximate analysis of the cassava peels prior to activation is shown in Table1. The peels were more of volatile matter but it contained an appreciable amount of fixed carbon which is required for adsorption. Analysis carried out so far on cassava peels were more of the nutritive aspect and much have not been done on the proximate based on the fixed carbon content [30]. However, the ash content of 4.8% was in close agreement with the analysis carried out by [30],[31].

Table 1: Proximate analysis result for cassava peels

Moisture (%)	Volatile (%)	Fixed Carbon (%)	Ash (%)
5.60	47.1	42.5	4.8

3.2. The Oxide analysis result for kaolin clay

The result of the oxide analysis of the clay is shown in Table2. The results were in close agreement with the oxide analysis of bentonite clay as analyzed by reference [19]. The high percentage of aluminum and silica supports that the substance is clay. Moreover, the low contents of metal ions supports that the clay is more of kaolinite [19].

Table 2: The oxide composition of kaolin clay

Oxide	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	MgO	K_2O	Na_2O	P_2O_5	SO_3	I.L
[%]	56.6	26.8	0.15	2.94	2.62	2.15	0.27	0.22	0.10	0.13	8.30

3.3. The effect of time and the kinetic parameters

From Tables3 and 4, it can be seen that the contact time was an important parameter in the adsorption process. Both the percentage removal of zinc ion and the adsorption capacity of the adsorbents were affected by the contact time. The percentage removal and the adsorption capacity increased with the increase in contact time. After 40minutes however, the equilibrium concentration became somewhat constant and consequently percentage removal and the activated carbon increase became insignificant. At this point, the equilibrium was attained. Reference [32] reported that the equilibrium of zinc adsorption on *Carica papaya* root powder was achieved after 50minutes contact at using 10mg/g initial concentration. Table5 shows the summary of the adsorption kinetic parameters for both the clay and the carbon. It can be seen that both the carbon and the clay kinetics were described by the pseudo second order kinetic model judging by the value of the coefficient of determination R^2. The pseudo second order kinetics assumes that the overall sorption rate is limited by the rate of sorbate diffusion in the pores of sorbent(intraparticle diffusion model) [33] .The kinetics parameters agreed with the report by [34], and [32] that zinc adsorption followed pseudo second order kinetics. The fitness of the data into the kinetic models are shown in Figures1and 2.

Table3: The effect of time on Adsorption of zinc using kaolinite clay

Time(min)	Volume(L)	Mass(g)	Co(mg/L)	Ce(mg/L)	%Removal	qt(mg/g)
10	0.02	0.2	32	15.20	52.50	1.68
20	0.02	0.2	32	12.50	60.94	1.95
30	0.02	0.2	32	11.00	65.63	2.10
40	0.02	0.2	32	8.90	72.19	2.31
60	0.02	0.2	32	8.80	72.50	2.32

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Table4: The effect of time on Adsorption of zinc using cassava peels activated carbon

Time(mins)	Volume(L)	Mass(g)	Co(mg/L)	Ce(mg/L)	%Removal	qt(mg/g)
10	0.01	0.1	32	13.10	59.06	1.89
20	0.01	0.1	32	11.20	65.00	2.08
30	0.01	0.1	32	8.70	72.81	2.33
40	0.01	0.1	32	6.30	80.31	2.57
60	0.01	0.1	32	5.98	81.31	2.60

Table5: The kinetic parameters for zinc adsorption on clay and carbon

Model	Parameter	Clay adsorption	Carbon adsorption
Pseudo First order	K1 $(\text{min})^{-1}$	0.130	0.073
Pseudo First order	qe calculated (mg/g)	3.893	2.028
Pseudo First order	qe observed (mg/g)	2.320	2.650
Pseudo First order	R^2	0.812	0.895
Pseudo second order	K2 (g/mg.min)	0.030	0.048
Pseudo second order	qe calculated (mg/g)	2.552	2.954
Pseudo second order	qe observed (mg/g)	2.320	2.650
Pseudo second order	R^2	0.998	0.996

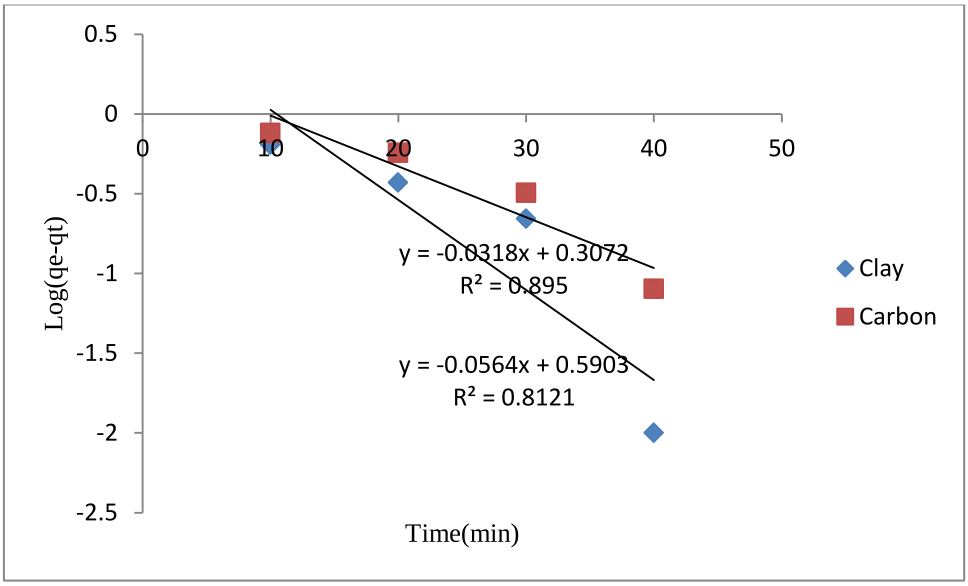

Figure.1: The pseudo first order kinetics for zinc adsorption on at room temperature

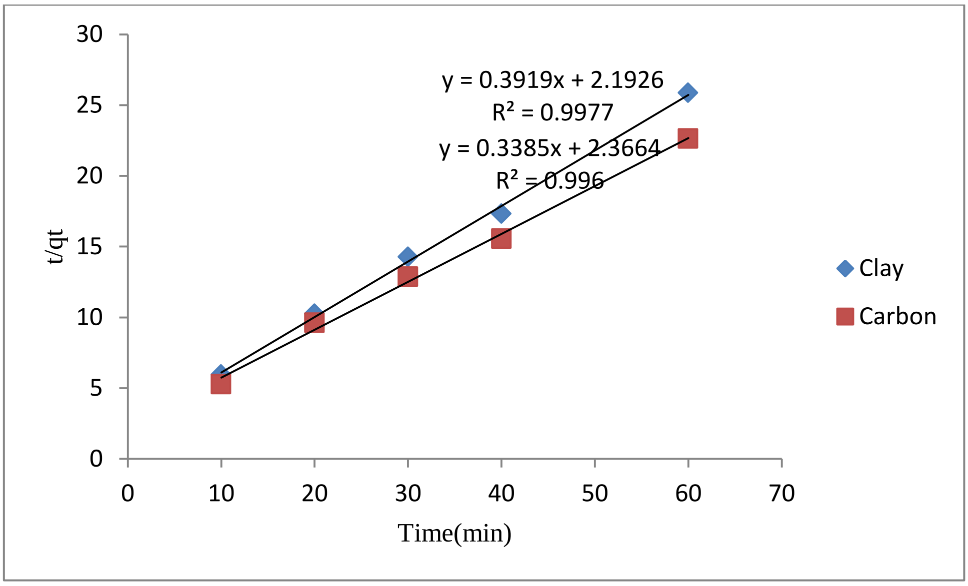

Figure 2: The pseudo second order kinetics for zinc adsorption at room temperature

3.4. The effect of concentration and the adsorption isotherms

Tables6 and 7 show that the initial concentration of zinc affected the percentage removal and the adsorption capacity. Whereas there was an inverse relationship between initial concentration and the percentage removal, the relationship between the initial concentration and the adsorption capacity was direct. At initial concentration of 10ppm, clay removed 95.1% of the zinc at equilibrium with adsorption capacity of 0.95mg/g while carbon removed 97.2% of the zinc with adsorption capacity of 0.97mg/g. At the initial concentration of 40ppm, clay removed 70% with adsorption capacity 2.8mg/g while carbon removed 90% with adsorption capacity of 3.6mg/g. It can be seen from Tables6 and 7 that the activated carbon gave higher adsorption capacity and percentage removal than the kaolin clay.

The summary of the parameters for the different adsorption isotherms is shown in Table8. It can be deduced that Langmuir, Freundlich and Temkin Isotherms provided good fit to the experimental data. The coefficient of determination values (R^2) were lie between 0.9 and 1.0 which are reasonable for good fitness. The implication is that both the cassava peels activated carbon and the kaolinite clay are microporous solids having relatively small external surface, and the limiting uptake being governed by the accessible micropore volume rather that by the internal surface area [25]. The monolayer adsorption models suggests that the adsorptions were more of chemisorptions [24]moreover, the values of the index n of the Freundlich isotherm being 2.99 and 2.0 for the clay and the carbon respectively indicates that the adsorptions were more of chemisorptions[7]. It was equally observed that zinc adsorption on activated carbon prepared from bamboo followed Langmuir and Freundlich iostherms at room temperature [7]. The adsorption constant b_T of the Temkin isotherm were 4393.8J/mol.K and 2623.3J/mol.K for the clay and carbon respectively. Reference [27] reported values of 5305J/mol.K and 5298J/mol.K for adsorption of phosphate on 10µm and 50µm cellulose membrane respectively.

Table6: Effect of initial concentration for adsorption of zinc on clay

Co(mg/L)	Volume(L)	mass(g)	Ce(mg/L)	%removal	qt(mg/g)
40	0.02	0.2	12.00	70.00	2.80
30	0.02	0.2	5.90	80.33	2.41
20	0.02	0.2	1.84	90.80	1.82
10	0.02	0.2	0.49	95.10	0.95

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Table7: Effect of initial concnetration for adsorption of zinc on carbon

Co(mg/L)	Volume (L)	mass(g)	Ce(mg/L)	%Removal	qt(mg/g)
40	0.01	0.1	4.00	90.00	3.60
30	0.01	0.1	2.10	93.00	2.79
20	0.01	0.1	1.41	92.95	1.86
10	0.01	0.1	0.28	97.20	0.97

Table8: Parameters for different adsorption isotherms of zinc adsorption of clay and carbon

	Langmuir adsorption isotherm	
	Clay	Carbon
ql(mg/g)	3.058	4.847
Kl(L/mg)	0.794	0.633
R^2	0.998	0.910
	Freundlich adsorption isotherm	
N	2.991	2.009
Kf(mg/g)	1.306	1.778
R^2	0.961	0.976
	Temkin adsorption isotherm	
b_T(J/mol.K)	4392.813	2623.286
A(L/g)	11.461	8.173
R^2	0.997	0.913

3.5. The effect of temperature and the thermodynamic parameters

Tables9 and 10 show the effect of temperature and the thermodynamic parameters for the adsorption of zinc on clay and carbon respectively. The adsorption capacity and the percentage removal increased with the increase in temperature. The thermodynamic data fitted into the thermodynamic model with the R^2 values lying between 0.9 and 1.0 as can be seen in Figure 3. The values of the change in enthalpy (ΔH) were positive showing that the process was endothermic. References [35], [36], and [37] reported endothermic process for zinc adsorption on different adsorbents. The ΔH for the adsorption of zinc on clay was 15.181KJ/mol while that of activated carbon was 77.918KJ/mol. According to reference [25], values of enthalpy change at 20-40KJ/mol shows physical adsorption and values at 40-400KJ/mol shows chemisorptions. It means that the zinc adsorption on the kaolinite clay was more of physical adsorption and the bonding force was more of van der waals force while the zinc adsorption on the cassava peels activated carbon was more of chemical adsorption and the binding force was chemical bond. Furthermore, the values of the ΔH show that adsorption on the clay was reversible and that on the carbon was irreversible. The values of the Gibb's free energy change (ΔG) were negative showing that the adsorption processes were spontaneous. The absolute values of the Gibb's free energy change for the adsorption on carbon were higher than the corresponding values for the adsorption on clay. This means that the adsorption on carbon was more spontaneous. The positive entropy changes (ΔS) show that the processes were feasible [25].

Table9: Thermodynamics parameters for zinc adsorption on clay

hTemp (°C)	Co (mg/L)	Ce (mg/L)	qt (mg/g)	%Removal	-ΔG (J/mol)	ΔS (J/mol.K)	ΔH (J/mol)
40	32	13.4	1.86	58.125	731		
50	32	12.4	1.96	61.250	1240	50	15181
60	32	12	2.00	62.500	1748		
70	32	10	2.20	68.750	2257		
75	32	9	2.30	71.875	2511		

Table 10: Thermodynamics parameters for zinc adsorption on carbon

Temp (°C)	Co (mg/L)	Ce (mg/L)	qt (mg/g)	%Removal	-ΔG (J/mol)	ΔS (J/mol.K)	ΔH (J/mol)
40	32	16	1.6	50	735		
50	32	15.5	1.65	51.56	1730	243	76734
60	32	4.5	2.75	85.93	4196		
70	32	2.8	2.92	91.25	6662		
80	32	2.1	2.99	93.44	7895		

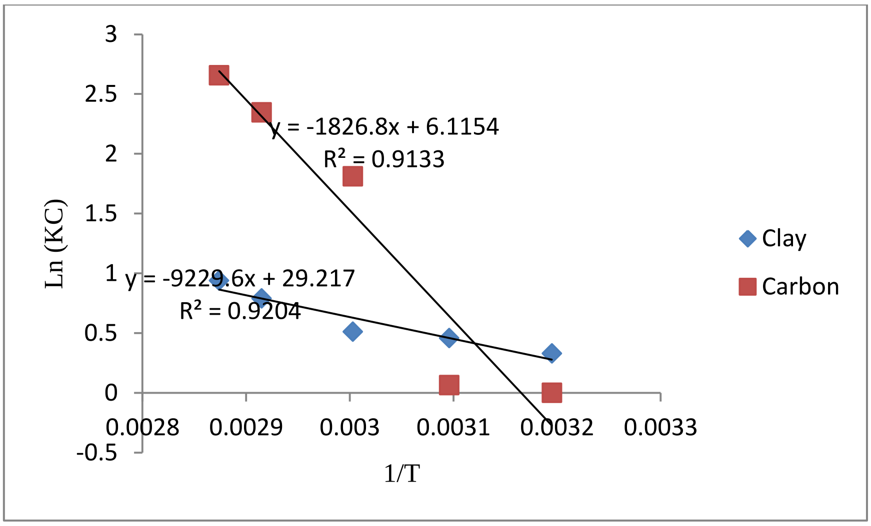

Figure .3: The thermodynamic model for zinc adsorption on clay and carbon

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3.6. The effect of pH on the adsorption process

Figure4 shows the effect of pH on clay and carbon adsorption respectively. The pH of the solution affected the adsorption capacity and the percentage removal due to surface charges interactions [38]. It can be seen that high adsorption capacity and percentage removal were recorded at pH around neutral point. The adsorption capacity at the alkaline region were however higher than that at the acidic region. The alkalinity improved the adsorption capacity of clay even beyond the adsorption capacity of carbon. Reference [39] reported that significant removal of zinc, cadmium and copper using clay minerals were recorded at pH above 6.0.

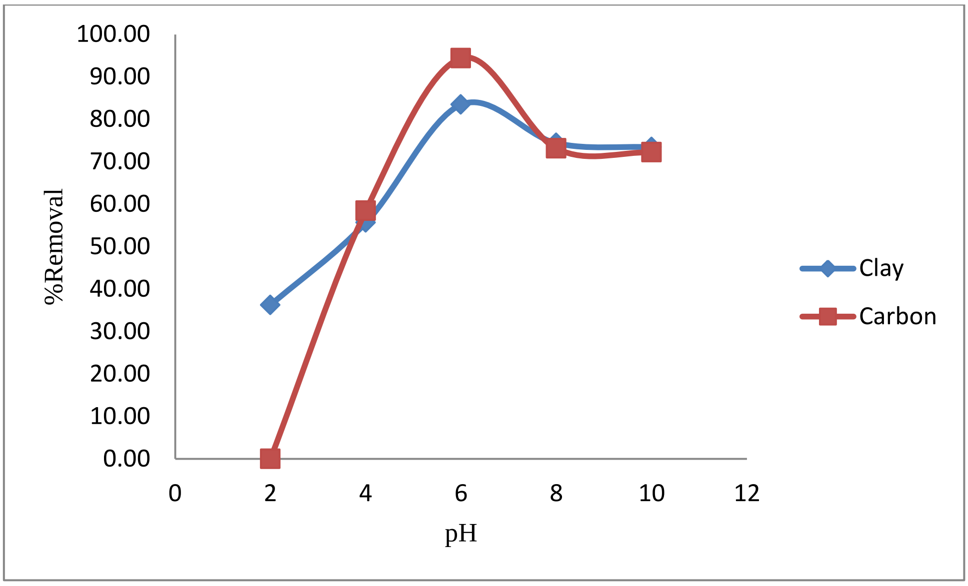

Fig.4: The effect of pH on zinc percentage removal

3.7. The effect of dosage on the adsorption process

It can be seen from Figures5 and 6 that the increase in dosage gave higher increase in percentage removal but the adsorption capacity decreased on both the carbon and the clay. The highest adsorption capacity was obtained with a dosage of 0.1g/20mL but the lowest percentage removal was equally obtained with this dosage. In choosing the best dosage for the rest of the experiment, both the percentage removal and the adsorption capacity were considered and that was the reason behind using the dosage of 0.2g/20mL. With 0.1g/20mL dosage, the carbon gave 5.1mg/g adsorption capacity while the clay gave 4.54mg/g adsorption Capacity. As the dosage increases, the percentage removal increases but the adsorption capacity decreases. However, the increase in percentage removal and the decrease in adsorption capacity became somewhat insignificant beyond a dosage of 0.2g/20mL

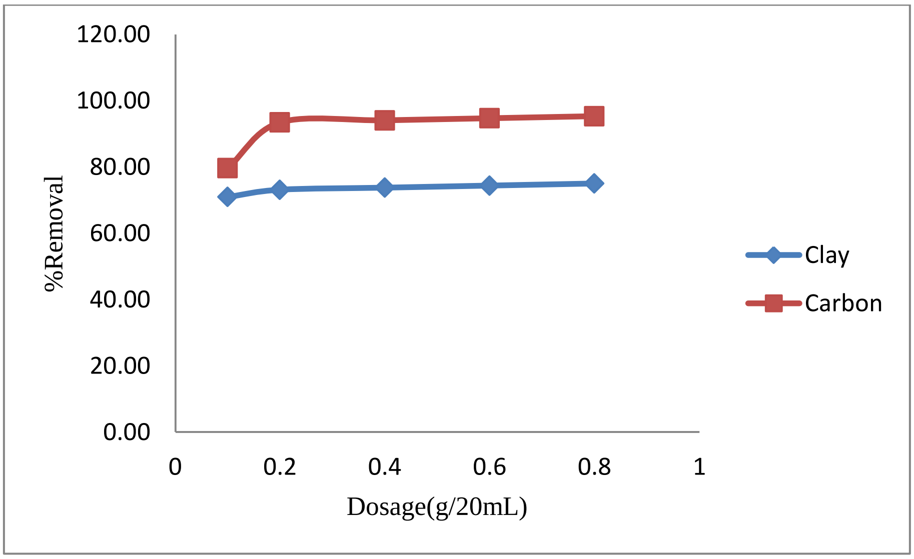

Fig.5: The effect of dosage on percentage removal

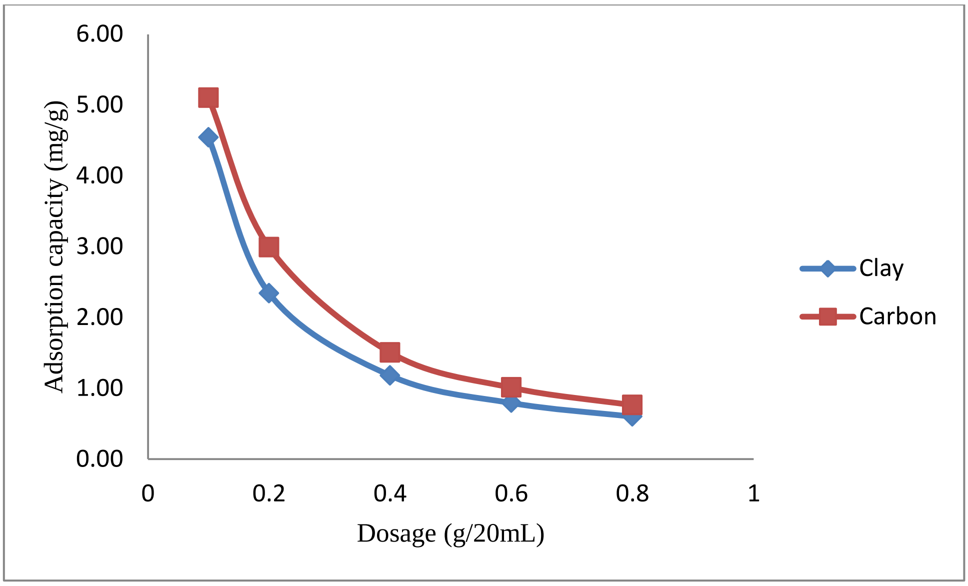

Fig.6: The effect of dosage on adsorption capacity

3.8. Optimization Study

The optimization of the process parameters for the adsorption of zinc ions using cassava peels activated carbon and kaolinite clay was carried out using the Box Behnken Design of Response Surface Methodology (RSM). The design parameters are shown in Table11. Using Design Expert (version 6.0.6), a total of 92 runs were generated and the response which is the percentage removal was obtained experimentally. Analysis of the response was also achieved using Design Expert. The Design Expert selected linear model as the adequate model for the system where the percentage removal is the response. The Analysis of Variance (ANOVA) showed that the model, the five numeric factors (time, temperature, pH, dosage and concentration) and the categorical factor (The type of adsorbent) were significant at 0.01significant level. The ANOVA table with the analysis parameters is shown in Table12. The R^2 value of 0.902 was in reasonable agreement with the predicted R^2 of 0.895 and the adjusted R^2 value of 0.883, which means that linear model is adequate for the system [40]. The linear model equations for the clay and carbon are shown in (20) and (21) respectively. Both equations have positive coefficients for time, temperature, pH and dosage. The coefficient of concentration in both equations is negative. This means that the overall effect of concentration on the percentage removal was negative. The percentage removal decreased with the increase in the initial concentration of zinc.

Table11: The optimization design parameters

Factor	Name	Units	Type	Low Actual	High Actual	Low Coded	High Coded
A	Time	Min	Numeric	10	60	-1	1
B	Temperature	°C	Numeric	30	70	-1	1
C	pH		Numeric	3	8	-1	1
D	Concentration	mg/L	Numeric	10	40	-1	1
E	Dosage	g/20mL	Numeric	0.1	0.8	-1	1
F	Type of adsorbent		Categorical	Clay	Carbon		

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Table12: The ANOVA table

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	Remarks
Model	4186.063	6	697.6770833	129.761	< 0.0001	significant
A	1128.125	1	1128.125	209.8201	< 0.0001	
B	205.0313	1	205.03125	38.13378	< 0.0001	
C	120.125	1	120.125	22.34206	< 0.0001	
D	144.5	1	144.5	26.87557	< 0.0001	
E	52.53125	1	52.53125	9.770292	0.0024	
F	2535.75	1	2535.75	471.6244	< 0.0001	
Residual	457.0136	85	5.376630435			
Lack of Fit	455.6803	75	6.075736715	45.56803	< 0.0001	significant
Pure Error	1.333333	10	0.133333333			
Cor Total	4643.076	91				
Std. Dev.	2.318756		R-Squared	0.901571		
Mean	72.79348		Adj R-Squared	0.894623		
C.V.	3.18539		Pred R-Squared	0.882819		

3.9. Mathematical model equations

$$\%\text{Removal(clay)} = 50.54 + 0.23 * \text{time} + 0.13 * \text{temp} + 0.78 * \text{pH} - 0.14 * \text{concentration} + 3.66 * \text{dosage} \quad (20)$$

$$\%\text{Removal(carbon)} = 61.03 + 0.24 * \text{time} + 0.13 * \text{temp} + 0.78 * \text{pH} - 0.14 * \text{concentration} + 3.66 * \text{dosage} \quad (21)$$

3.10. The numerical optimum solution

The numerical optimum solution containing the optimum values for the adsorption using clay and carbon is shown in Table13. The optimum percentage removal of zinc using carbon was significantly higher than that of clay. The optimum time was almost the same for both adsorbents. The optimum temperature using clay was higher than that of carbon. Optimum pH using carbon was towards the acidic region while the optimum for the clay was towards the alkaline region.

Table13: The numerical optimum solution

Time(min)	Temp(°C)	pH	Concentration(ppm)	Dosage(g/20mL)	Type of adsorbent	%Removal
59.53	62.34	6.42	13.34	0.55	Carbon	88.1534
60.00	69.44	8.00	10.10	0.70	Clay	80.9108

4. CONCLUSION

Adsorption of zinc from aqueous solution was achieved using cassava peels activated carbon and untreated kaolinite clay. Factors such as contact time, temperature, pH, adsorbent dosage and initial metal concentration affected the adsorption significantly. The pseudo second order kinetics model provided a good fit to the kinetic data of the adsorption. The Langmuir, Freundlich and Temkin adsorption isotherms also provided good fit to the adsorption at room temperature. The thermodynamic analysis showed that the process was endothermic and spontaneous. The values of the heat of the adsorption suggested that the adsorption with clay was more of physical adsorption while that of carbon was more of chemical adsorption. The optimization study revealed that linear model was adequate for the system using the percentage removal as the response and that the percentage removal of zinc using cassava peels activated carbon was significantly higher than that of kaolin clay.

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