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## Enhanced Sorption of Trivalent Chromium unto Novel Cassava Peel Modified Kaolinite Clay

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### ABSTRACT

The wide use of chemicals in modification of kaolinite in order to improve its adsorption capacity is expensive, requires skilled personnel, noxious to the environment and results in secondary contamination. As a result this study investigated an eco and environmental friendly modification of kaolinite using cassava peel to enhance its adsorption for Cr (III) ions. The adsorption capacity of the Unmodified Kaolinite Clay (UKC), Cassava Peel Modified Kaolinite Clay (CPMKC) and Unmodified Cassava Peel (UCP) were compared. The effect of experimental variables such as pH, Cr (III) ion concentration, adsorbent dosage, particle size, agitation time and temperature on sorption was studied using batch methodology. Equilibrium isotherm studies was analyzed by the Langmuir, Freundlich and Halsey isotherm models while the Pseudo First Order (PFO), Pseudo Second Order (PSO) and Intraparticle Diffusion (IPD) models were used for kinetic analysis. All the experimental variables were found to have significant effect on Cr (III) ions sorption on the adsorbents with an optimum pH of 5.0, adsorbent dose 0.1 g, particle size 100  $\mu\text{m}$  and chromium concentration of 375 mg/L obtained. Equilibrium sorption at 25, 20 and 60 min was obtained for UKC, CPMKC and UCP respectively which showed the faster sorption potential of CPMKC. The Langmuir model had the best fit with linear regression ( $R^2$ ) of 0.991 and 0.998 for UKC and UCP. The Freundlich and Halsey models gave the best fit with same  $R^2$  of 0.975 for CPMKC and the Sum of Square of Errors (SSE) was slightly lower for the Freundlich (0.833) than the Halsey (0.897). The PFO model gave the best fit ( $R^2 > 0.980$ ) and lowest SSE than the PSO model. An initial sorption rate  $h$  (mg/g min) of 2.16, 3.14 and 1.02 was obtained for UKC, CPMKC and UCP respectively. Thermodynamics revealed an endothermic physical sorption of Cr (III) on all the adsorbents. The sorption was in the order UCP > CPMKC > UKC, which showed the suitability of cassava peel in enhancing the sorption ability of kaolinite for chromium ion from aqueous solution.

**Keywords:** Cassava peel, Kaolinite, Heavy metals, Isotherm, Kinetic, Thermodynamic

### INTRODUCTION

Chromium containing compounds are widely utilized in most industrial processes leading to the discharge of the waste generated into the environment. Therefore certain amount of chromium is transported from the industrial effluent into receiving water bodies. Chromium although essential in certain trace amounts by living organisms could be harmful at high concentrations due to its persistence, non-biodegradability and bioaccumulation tendency [1]. Although Cr (III) is not as toxic as Cr (VI), it should be removed from wastewaters since it can easily be oxidized in the environment to Cr (VI) [2]. Many removal techniques such as ion exchange, filtration, precipitation, coagulation and solvent extraction have been utilized but have the disadvantage of high cost and low efficiency [3]. Adsorption using activated carbon is the most efficient method but is expensive which led to the use of many low cost materials for removal of chromium from solution [4]. Kaolinite clay as a low cost material has been reported to have low adsorption capacity than biomass materials due to its relatively low surface area usually less than 20  $\text{m}^2/\text{g}$  [5]. The widely utilized acid and alkaline modification has been found to improve the adsorption potential of kaolinite for heavy metal but it is expensive, requires skilled personnel, noxious to the environment and results in secondary contamination.

Hence the need to exploit other treatment techniques. Recently, it was reported that modification of montmorillonite clay with rice husk improved its adsorption capacity for heavy metals significantly [6]. It is therefore possible that modification of kaolinite with biomass materials could also improve the adsorption capacity. Cassava peel as a low cost and ecofriendly material has been reported to have high uptake potential for chromium ions [7] but has not been applied in the modification of kaolinite. This study therefore exploits the use of cassava peel in treatment of kaolinite for the sequestration of Cr (III) ions from contaminated aqueous solution.

## METHODOLOGY

### Sorbents preparation

The kaolinite clay was obtained from Aloji in Kogi State Nigeria and 1 kg was dispersed in excess distilled water in a pretreated plastic container. The clay was stirred and left for 48 h to settle after which excess water was decanted. The residue was sundried for two weeks and dried in an oven at 105°C for 1 h then pulverized and passed through 100-500 µm mesh sieves to obtain the Unmodified Kaolinite Clay (UKC). The cassava was obtained from a local market (Orie) Emene, Enugu, Nigeria and washed with excess water to remove surface impurities. The peel was then sliced by the use of a kitchen knife and cut into smaller pieces then sundried for 3 weeks. The dried peels were then oven dried at 70°C for 3 h, pulverized and passed through mesh sieves of sizes 100-500 µm to obtain the Unmodified Cassava Peel (UCP). The kaolinite modified with cassava peel was prepared by mixing equal weight of UKC and UCP, after which little amount of distilled water was added and mixed thoroughly. The mixture was pounded using a mortar and pestle to enable proper blending. The solid paste was then separated into smaller sizes and sundried for 1 week after which it was oven dried at 70°C for 2 h. The dried cake was then pulverized and passed through 100-500 µm mesh sieves to obtain the Cassava Peel Modified Kaolinite Clay (CPMKC).

### Adsorbate preparation

Chromium (III) nitrate nonahydrate ( $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ) was obtained from Sigma-Aldrich and utilized without any purification. The adsorbate solution of  $\text{Cr}^{3+}$  ion was prepared by dissolving known amounts of  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  in distilled water to obtain a solution of concentration 500 mg/L. Several solutions of lower concentrations ranging from 75 to 375 mg/L were prepared from the stock solution by serial dilution. The pH of the solutions were adjusted to values ranging from 2.0 to 8.0 by the addition drop wise of 0.1 M  $\text{HNO}_3$  or 0.1 M  $\text{NaOH}$  which was checked by the use of a pH meter (Mettler Toledo, Model MP 220).

### Sorption experiments

The sorption study was performed by batch methodology to investigate the effect of pH (2.0-8.0), Chromium ion concentration (75-375 mg/L), adsorbent dosage (0.1-0.5 g), adsorbent particle size (100-500 µm), agitation time (5-120 min) and temperature (300-323 K). This was performed by contacting 0.1 g of the adsorbent with 50 mL of the adsorbate in a 100 mL pretreated plastic container at room temperature. The mixture was agitated in a shaker at 200 rpm at the given contact time of 120 min at room temperature of 300 K. A thermo-stated water bath was utilized when the effect of temperature was studied. To determine the effect of a particular parameter on sorption that parameter was varied while others were kept constant at the optimum conditions of pH 5.0, particle size 100 µm and Cr (III) ion concentration of 375 mg/L. At the end of a given time of agitation, the solutions were filtered and the amounts of Cr (III) ions remaining in solution were determined by the Atomic Absorption Spectrophotometer (AAS) (Buck scientific model 210 VGP). The percentage sorption and uptake capacity  $q_e$  (mg/g) were calculated from the following equations respectively:

$$\% \text{ Sorption} = 100[(C_o - C_e)/C_o] \quad (1)$$

$$q_e = v(C_o - C_e)/m \quad (2)$$

Where  $C_o$  (mg/L) and  $C_e$  (mg/L) represents the initial and equilibrium concentrations of Cr (III) ion in solution,  $v$  (L) and  $m$  (g) corresponds to the volume of adsorbate and mass of adsorbent used respectively.

### Error analysis

Sum of Square of Errors (SSE) was applied to help identify the best fitted isotherm or kinetic models applied to the sorption process due to the inherent bias resulting from linearization using the linear regression ( $R^2$ ). The SSE is given by the equation [8]:

$$SSE = \sum (q_{ecal} - q_{exp})^2 \quad (3)$$

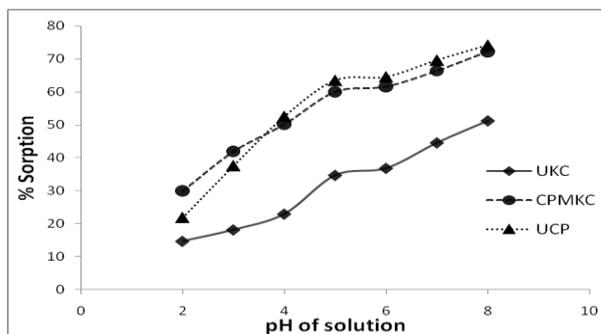
Where  $q_{exp}$  (mg/g) and  $q_{ecal}$  (mg/g) represents the experimental uptake capacity and that calculated from the model respectively. The smaller the SSE the better fit of the model. This was calculated with the help of the Microsoft excel solver add-on software.

## RESULTS AND DISCUSSION

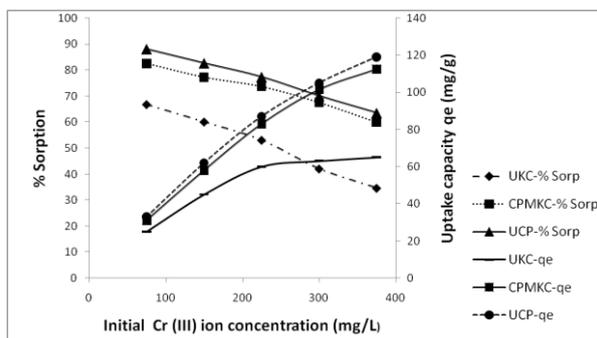
### Effect of adsorption variables

The influence of pH on the sorption of chromium onto the adsorbents was performed because the pH affects the surface active sites responsible for metal ion binding. Figure 1 shows the effect of initial solution pH on the sorption of Cr (III) ions on the adsorbents. It was observed that a steady increase in adsorption with increase in pH from 2.0 to 8.0 was recorded. Optimum adsorption of Cr (III) ion on the adsorbents was obtained at pH 5.0 and the higher adsorption obtained with further increase in pH from 6.0 to 8.0 is due to the precipitation of hydroxide forms of chromium [4]. The pH of 5.0 was then utilized in the sorption study in order to avoid precipitation of Cr (III) ions. The increase in sorption with increase in pH was simply as a result of decreased competition between chromium ions and protons for the active sites of the adsorbents [9]. The same trend of the influence of pH obtained has been reported [10].

The initial metal ion concentration is an important factor in adsorption study because it determines the amount of metal ions present in solution and subsequently that sorbed by the adsorbent. The effect of initial Cr (III) ion concentration on adsorption by the adsorbent is shown in Figure 2. A decrease in percentage adsorption with increase in initial Cr (III) ion concentration on all the adsorbents was obtained. This decrease was as a result of saturation of the active sites of the adsorbents at higher metal concentrations leading to less removal of chromium ions from solution. At low concentrations, more of chromium ions would be removed by the abundant active sites on the adsorbents [11]. A reverse trend was also observed in Figure 2 in which an increase in uptake capacity of the adsorbents for chromium ions with increase in chromium concentration was obtained. This increase has been attributed to high concentration gradient which resulted in more chromium ions fixed on the adsorbent resulting in optimum utilization of the active sites [12]. An initial Cr (III) ion concentration of 375 mg/L was utilized in the sorption experiments since maximum occupation of the active sites of the adsorbents was obtained. Furthermore, it was observed from both Figures 1 and 2 that the sorption of Cr (III) ions on the adsorbents was in the order UCP>CPMKC>UKC. This indicated that the cassava peel was effective in enhancing the adsorption capacity of the kaolinite clay at all pH and metal concentration range studied but not vice versa. However, CPMKC recorded a higher sorption of Cr (III) than UCP at low pH values of 2.0 and 3.0 which indicated the effectiveness of this new adsorbent in the sorption of chromium ions even at low pH values which is desirable.

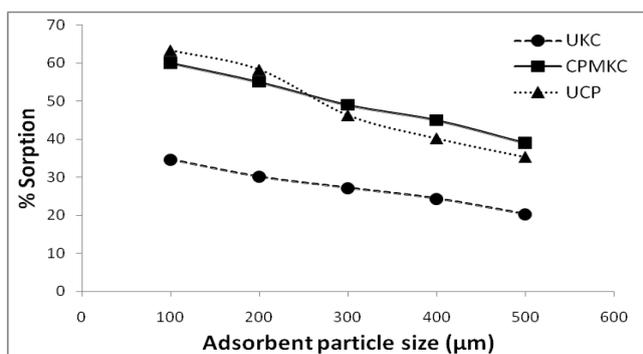


**Figure 1: Effect of initial solution pH on the sequestration of Cr (III) ions on the adsorbents**



**Figure 2: Effect of initial chromium (III) ion concentration on its sorption on the adsorbents**

The effect of adsorbent particle size on the sorption of Cr (III) ions on the adsorbents is shown in Figure 3. From the graph it was clearly seen that a decrease in adsorption on all the adsorbents with increase in adsorbent particle size was recorded. The decrease is attributed to decrease in surface area of the adsorbent with increase in particle size [9]. A very significant deduction is that at larger particle sizes of 300-500 μm, CPMKC showed a higher adsorption of chromium ions than UCP. This indicated that our new adsorbent would be more effective in sorption of Cr (III) ions at larger particle sizes, probably due to the finer particles of kaolinite when passed through mesh sieves of larger sizes than cassava peel. The adsorbent particle size of 100 μm was employed in this study due to its optimum sorption ability.



**Figure 3: Effect of adsorbent particle size on the sorption of Cr (III) ions from solution by the adsorbents**

The influence of adsorbent dose on the sorption of Cr (III) on the adsorbents is presented in Figure 4. An increase in percentage adsorption with adsorbent dose on all the adsorbents was observed. The trend of absorption at all adsorbent doses was also in the order UCP>CPMKC>UKC. The increase is due to an increase in the number of active sites available for sorption of Cr (III) ions with increase in adsorbent dosage [4]. On the other hand, a decrease in the uptake capacity of the adsorbents for Cr with increase in dosage was recorded. This is simply due to the fact that the same concentration of Cr (III) ions in solution is sorbed by an increasing concentration of adsorbent dosage having more active sites, resulting in the active sites becoming unsaturated [13]. Therefore the adsorbent dose of 0.1 g was chosen in this experiment in which maximum utilization of the active sites of the adsorbents was obtained. In order to obtain both high adsorption capacity and percentage adsorption by the adsorbent, the adsorbent should be implemented in several sorption units in parallel rather than in a single large unit. Similar trend have been reported by other scientist [14,15].

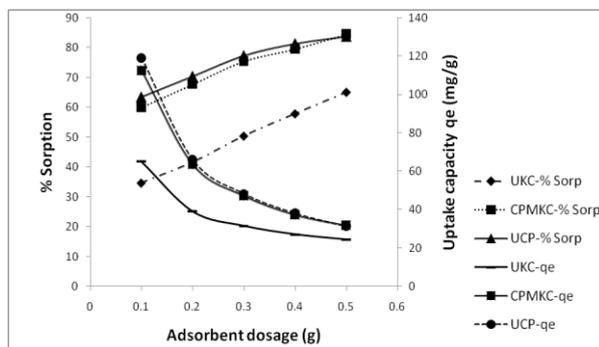


Figure 4: Effect of adsorbent dose on the sequestration of Cr (III) ions from solution by the adsorbents

The influence of initial solution temperature on the percentage adsorption of Cr (III) ions on the adsorbents is illustrated in Figure 5. An increase in sorption with temperature increase from 300 to 323 K was obtained for all the adsorbents. UCP also recorded the highest sorption than other adsorbents at all temperatures. The enhanced sorption of Cr (III) ions by the adsorbents with temperature increase is attributed to the ability of chromium ions to overcome resistance to mass transfer with increase in kinetic energy to undergo an interaction with the active sites of adsorbents [16]. The trend indicated an endothermic adsorption process on the adsorbents.

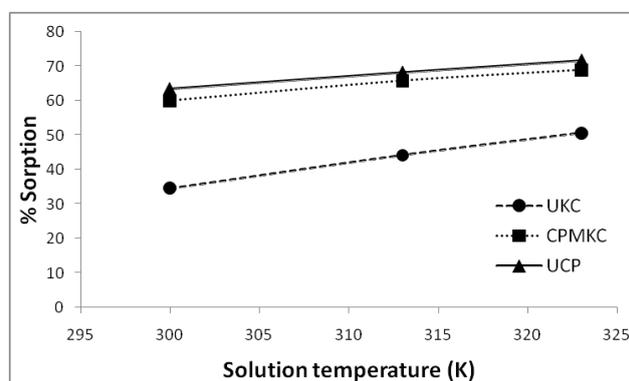


Figure 5: Effect of solution temperature on the sorption of Cr (III) ions from solution on the adsorbents

A good adsorbent must not only have a high sorption capacity but also a fast rate of removal. In this regard, the effect of agitation time on the sorption of Cr (III) ions on the adsorbents is shown in Figure 6. An increase in adsorption with increase in time was achieved after which the removal became constant attaining equilibrium. Different equilibrium agitation times of 20, 25 and 60 min were achieved for CPMKC, UKC and UPC respectively. It has been reported that the nature of the adsorbent and its active sites determine the rate at which equilibrium is attained [17].

This implied that the active sites of CPMKC enabled a fast sorption of Cr (III) ions compared to the other adsorbents which is desirable. The fast sorption on CPMKC indicated the applicability of the adsorbent in industrial processes. In general, the initial increase in sorption with time is due to the presence of abundant active sites at the start of the process for effective removal of Cr (III) ions. As time progresses, the active sites become used and get saturated consequently attaining equilibrium [11]. A contact time of 120 min was utilized in all the sorption experiment in this study to enable equilibrium attainment on all the adsorbents. Similar trend of increase in sorption with time until equilibrium have been reported by many researchers [2,4,8,18].

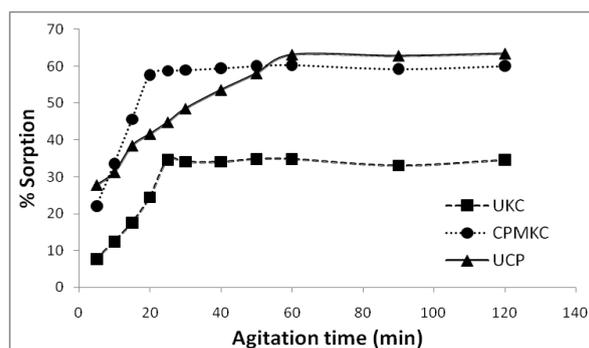


Figure 6: Effect of agitation time on the sorption of Cr (III) ions from solution by the adsorbents

### Sorption isotherm

Sorption isotherms such as the Langmuir, Freundlich and Halsey were applied to determine the affinity between the adsorbents and Cr (III) ions. The Langmuir isotherm is based on a monolayer sorption on homogenous surface of the adsorbent. The linear form of the Langmuir isotherm model is expressed as Nouacer *et al.* [10]:

$$C_e/q_e = 1/(q_L K_L) + C_e/q_L \quad (4)$$

Where  $K_L$  (L/mg) and  $q_L$  (mg/g) represents the Langmuir constant and monolayer sorption capacity respectively and are presented in Table 1. From the result it was observed that the linear regression coefficient ( $R^2$ ) obtained for UKC and UCP were very high ( $>0.990$ ) which suggested that both adsorbents were made up of homogenous active sites involving monolayer sorption of Cr (III) ions. A very important Langmuir separation factor ( $R_L$ ) was used to determine if the sorption process is favorable ( $R_L < 1$ ) or unfavorable ( $R_L > 1$ ) and is represented as Nharingo *et al.* [12]:

$$R_L = 1/[1 + K_L C_0] \quad (5)$$

The value of  $R_L$  for the sorption of Cr (III) ions on all the adsorbents was in the range of 0.093-0.426 which suggested a favorable adsorption between the adsorbents and Cr (III) ions.

Table 1: Equilibrium isotherm model parameters for the sorption of Cr (III) ion from solution

Isotherm models	UKC	CPMKC	UCP
<b>Langmuir</b>			
$q_L$ (mg/g)	83.3	156.7	156.7
$K_L$ (L/mg)	0.021	0.018	0.026
$R^2$	0.991	0.975	0.998
SSE	1.874	8.325	0.732
<b>Freundlich</b>			
$K_F$ (mg/L) <sup>1/n</sup>	7.23	8.26	12.45
$n$	2.37	1.85	2.11
$R^2$	0.902	0.997	0.98
SSE	12.327	0.883	4.373
<b>Halsey</b>			
$n_H$	-2.37	-1.85	-2.11
$K_H$	0.009	0.02	0.005
$R^2$	0.902	0.997	0.98
SSE	12.789	0.897	4.315

The Freundlich isotherm on the other hand represents a multilayer adsorption on a heterogeneous surface of the adsorbent and is expressed linearly as [4]:

$$\log q_e = \log K_F + [1/n] \log C_e \quad (6)$$

$K_F$  (mg/g) and  $n$  are the Freundlich constants representing adsorption capacity and intensity and are given in Table 1. The  $R^2$  values obtained for UKC and UCP were lower than that of the Langmuir isotherm, while that of CPMKC was higher (0.997) which indicated a heterogeneous surface. The heterogeneous nature of CPMKC must have resulted from the mixing of cassava peel and the kaolinite which incorporated different types of active sites. However, the SSE values should also be considered to validate the best fitted isotherm to the sorption process. The SSE also corroborated the  $R^2$  analysis, recording the lowest errors of 1.874 and 0.732 for the Langmuir isotherm for UKC and UCP and the lowest value of 0.883 for the Freundlich model on CPMKC. Also,  $n$  values between 1 and 10 obtained for all the adsorbents indicated a favorable adsorption of Cr (III) ions by all the adsorbents as also deduced previously from the Langmuir  $R_L$  value [9].

The Halsey model which also predicts a multilayer sorption on a hetero-porous adsorbent surface was applied to verify the applicability of the Freundlich model and is expressed in its linear form as:

$$\ln q_e = \ln K_H / n_H - [1/n_H] \ln C_e \quad (7)$$

Where  $K_H$  and  $n_H$  are the Halsey isotherm constants given in Table 1. It was observed that the  $R^2$  values obtained for Cr (III) sorption on all the adsorbents were exactly the same as those of the Freundlich isotherm. Also the magnitude of  $n$  and  $n_H$  were the same except that those of the later were negative. However looking at the SSE for both models, a very slight and insignificant difference was also obtained. The result of this study clearly indicated that both the Freundlich and Halsey isotherm would always have the same fit to adsorption data and depicts multilayer heterogeneous sorption. It is therefore not necessary to apply both models in a particular study but any of them can be applied to get the required information or fit. The good fit of the Halsey isotherm to the sorption of Cr (III) ions on CPMKC indicated that the heterogeneous surface comprises of both macro and micro pores [12].

### Kinetic analysis

The data generated from the influence of agitation time was fitted into three kinetic models namely; Pseudo First Order (PFO), Pseudo Second Order (PSO) and Intraparticle Diffusion (IPD) rate equations. The PFO model assumes that one metal ion is adsorbed on one active site of the adsorbent and is expressed linearly as:

$$\ln(q_e - q_t) = \ln q_e - K_1 t \quad (8)$$

Where  $q_e$  (mg/g) and  $q_t$  (mg/g) represent the sorption capacity at equilibrium and time  $t$  (min) respectively.  $K_1$  ( $\text{min}^{-1}$ ) is the PFO rate constant. The values obtained from the PFO model are given in Table 2. It is observed from the high  $R^2$  and low SSE values that the PFO model presented a good fit to the sorption of Cr (III) ions on all the adsorbents. The good fit obtained by the PFO model implied that the adsorption of Cr (III) ions was dependent on the concentration gradient and hence it was a diffusion controlled process which could be attributed to a physical sorption mechanism [4].

The PSO model assumes that chemisorptions is the rate controlling mechanism of the sorption process and is expressed linearly as:

$$t/q_t = 1/K_2 q_e^2 + t/q_e \quad (9)$$

Where  $K_2$  (g/mg min) is the PSO rate constant. The initial sorption rate,  $h$  (mg/g min) was also calculated from the equation:

$$h = K_2 q_e^2 \quad (10)$$

The PSO rate values are given in Table 2 and showed lower  $R^2$  and higher SSE values than the PFO model. This indicated that this model did not give a good fit to the sorption process as well as the PFO model and suggested that chemisorptions is not the rate controlling mechanism of Cr (III) ion sorption on the adsorbents. Also the initial sorption rate  $h$  (mg/g min) showed a faster rate of sorption on CPMKC (3.14) followed by UKC (2.16) and a slower rate on UCP (1.02) which clearly corroborated the equilibrium times obtained when the effect of agitation time was discussed.

The diffusion mechanism was analyzed by the use of the Intraparticle Diffusion (IPD) model equation presented linearly as:

$$q_t = K_d t^{1/2} + C \quad (11)$$

Where  $K_d$  ( $\text{mg/g min}^{1/2}$ ) is the IPD rate constant and  $C$  is the intercept which represent the boundary layer effect. IPD is the only rate controlling step of the sorption process if the plot is linear and passes through the origin with  $R^2$  value of one, otherwise it is not. From Table 2, the good  $R^2$  values ( $>0.95$ ) obtained for all the adsorbents showed the occurrence of IPD mechanism in the sorption of Cr (III) ions on the adsorbents, although it was not the only rate controlling mechanism. The occurrence of the intercept indicated the existence of some boundary layer effect or film diffusion mechanism in the sorption process. Similar results have been reported by some researchers [5,11,12].

Table 2: Kinetic rate model parameters for the sorption of Cr (III) ion from solution

Kinetic Models	UKC	CPMKC	UCP
<b>Pseudo-First order</b>			
q <sub>e</sub> (mg/g)	47.5	94.8	99.3
K <sub>1</sub> (min <sup>-1</sup> )	0.13	0.18	0.02
R <sup>2</sup>	0.992	0.989	0.983
SSE	0.813	0.639	1.243
<b>Pseudo-second order</b>			
h (mg/gmin)	2.16	3.14	1.02
K <sub>2</sub> (g/mgmin)	4.8 × 10 <sup>-3</sup>	8.04 × 10 <sup>-4</sup>	2.1 × 10 <sup>-4</sup>
q <sub>e</sub> (mg/g)	21.3	62.5	69.3
R <sup>2</sup>	0.99	0.982	0.975
SSE	2.832	4.914	3.715
<b>Intraparticle Diffusion</b>			
K <sub>d</sub> (mg/gmin <sup>1/2</sup> )	1.45	3.87	4.32
C	4.13	8.34	8.09
R <sup>2</sup>	0.975	0.967	0.977

### Thermodynamic analysis

The information regarding the feasibility, spontaneity and heat change of the sorption process were determined from the free energy change ( $\Delta G^0$ ), enthalpy change ( $\Delta H^0$ ) and entropy change ( $\Delta S^0$ ) thermodynamic parameters. The  $\Delta G^0$  value is related to the thermodynamic equilibrium constant by the equation:

$$\Delta G^0 = -RT \ln K_c \quad (12)$$

Where  $K_c = C_d/C_e$ ,  $C_d$  (mg/L) is the equilibrium concentration of Cr (III) ion adsorbed,  $T$  (K) is the absolute temperature and  $R$  (8.314 J/mol K) is the gas constant. The equilibrium constant  $K_c$  is also related to the  $\Delta H^0$  and  $\Delta S^0$  by the van't hof equation:

$$\ln K_c = -(\Delta H^0/RT) + (\Delta S^0/R) \quad (13)$$

The values of the thermodynamic parameters obtained are given in Table 3. It was observed that positive  $\Delta G^0$  values were obtained at 300 and 313 K for Cr (III) ion sorption on UKC which indicated a non-spontaneous process. However, at higher temperatures of 323 K and at all temperatures for CPMKC and UCP negative  $\Delta G^0$  values were obtained indicating a spontaneous process. This implies that the addition of cassava peel to kaolinite tend to make its adsorption spontaneous which is desirable. Also, the changes in  $\Delta G^0$  increased with increase in temperature meaning that higher temperature favor the adsorption process making it to be more spontaneous.

Positive values of  $\Delta S^0$  obtained indicated an increase in randomness of Cr (III) ions in solution and its interaction with the adsorbents. Positive  $\Delta H^0$  values obtained for sorption on all the adsorbents suggested an endothermic process which supported the increase in sorption with temperature obtained in Figure 5. An opposite result was observed in the biosorption of Cr (III) ions on *Citrullus lanatus* rind [4]. This is because the active sites of adsorbents have different surface properties and hence ways of interacting with metal ions. Significantly, values of  $\Delta H^0$  in the range 2.1-20.9 kJ/mol and 80-200 kJ/mol correspond to physisorption and chemisorptions respectively [19]. The  $\Delta H^0$  values obtained for CPMKC and UCP was 14.0 and 13.24 kJ/mol respectively, which indicated a physical sorption process, while that of UKC was slightly above 20.9 but far less than 80 kJ/mol suggesting a physicochemical sorption process mainly dominated by physisorption. Also, the fact that no value of sorption was within the range of 80-200 kJ/mol indicated that the sorption of Cr (III) ions on all the adsorbents is clearly not chemisorptions. This result corroborated the analysis obtained from the good fit of the PFO model and was the reason the kinetic data did not fit the PSO model. This physical adsorption is desirable for easy desorption and reuse of the sorbents [5]. Similar result was reported in the biosorption of heavy metals on *Adansonia digitata* root powders [20].

Table 3: Thermodynamic parameters for the sorption of Cr (III) ions from solution

Adsorbents	Temp (K)	$\Delta G^0$ (kJ/mol)	$\Delta H^0$ (kJ/mol)	$\Delta S^0$ (J/molK)
UKC	300	1.58	23.2	72.1
	313	0.59		
	323	-0.07		
CPMKC	300	-1.01	14	50.1
	313	-1.71		
	323	-2.16		
UCP	300	-1.38	13.24	48.73
	313	-1.99		
	323	-2.5		

## CONCLUSION

This study showed that the modification of kaolinite with cassava peel improved its sorption potential for Cr (III) ions from aqueous solution. However the unmodified cassava peel still recorded a slightly higher adsorption than the cassava peel modified kaolinite. The effect of pH, initial chromium ion concentration, adsorbent dose, particle size, agitation time and temperature were found to affect the adsorption on all the adsorbents significantly. The Langmuir isotherm presented the best fit for Cr (III) sorption on the kaolinite and cassava peel indicating a monolayer sorption on homogenous adsorbent surface. On the other hand the Freundlich and Halsey models gave the best fit for sorption on the cassava peel modified kaolinite which indicated a heterogeneous surface of the adsorbent. It was deduced that the Freundlich and Halsey models always presented the same linear regression coefficient but a slight difference was obtained from the sum of the square of errors. The pseudo first order model was found to present the best fit than the pseudo second order model for sorption on all the adsorbents. Intraparticle diffusion was found to contribute to the sequestration of Cr (III) ions by the adsorbents. Interestingly, the cassava peel modified kaolinite recorded the fastest sorption than the kaolinite and cassava peel which is desirable. Thermodynamics revealed an endothermic and physical adsorption process with an increase in randomness at the solid solution interface. However, even though desorption studies was not performed the low enthalpy values in physisorption range implied easy desorption of Cr (III) ions when regeneration of the adsorbents is required. This study therefore showed that cassava peel can be applied in the modification of kaolinite as an alternative to chemical modification.

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