

## REMOVAL OF CHROMIUM (VI) FROM DYE EFFLUENT USING NATURAL AND MODIFIED KAOLINITE CLAY.

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### ABSTRACT

*The utilization of chromium as antifouling agent in chrome-plating has resulted to pollution of water bodies. The adsorption of Cr (VI) from dye effluent was investigated using Ahoko kaolinite clay as an adsorbent. The kaolinite clay was characterized using X-ray diffraction (XRD), Brunauer Emmett and Teller (BET) and Scanning electron microscopy (SEM). XRD spectra showed that with modification there were shifts in the peaks for the modified clay. SEM indicated an increase in the porosity of the modified clay as compared to the unmodified clay, which enhanced metal ion adsorption. The BET indicated increase in the surface area and total pore volume of the kaolinite clay. The adsorption was studied with variation of time, temperature and adsorbent dosage at pH of 6. The equilibrium data were evaluated using Freundlich, Langmuir and Temkin, however, Freundlich have better fitting compared to the others. The kinetic study reveals that the pseudo-second-order show a very good fit for all reaction time at different initial concentrations.*

**Keywords:** Isotherm, Dye, Effluent, Clay, Thermodynamics, Kinetics, Adsorption, Cr (VI)

### 1. Introduction

Water pollution which is as a result of effluents disposal containing heavy metallic ions continues to be a matter of global concern, due to their deleterious nature. Since all polluted industrial and domestic wastewater finally return to the land and/or the waters, the topics relating to removal and treatment of wastewater remain relevant [1]. The last few decades have witnessed increased release of heavy metallic ions to the ecosystem which is due to industrialization. This has resulted in many adverse effects and obvious concerns globally; due to their harmful and deleterious effects on the health and well being of living organisms especially humans [2]. Many of the deleterious metallic ions are contained in industrial wastewater, and they include cadmium, chromium, nickel, zinc, lead, and copper occurring in various industrial activities ranging from geological activities, batteries production, paint production, leather tanning, electroplating, metal coating, and metal finishing [3]. Hence, the adsorption of hazardous metallic ions such as chromium from the environment is imperative due to the consciousness of the effects caused by pollution of the ecosystem by these metals.

The utilization of chromium has prevailing industrial applications as antifouling agent in cooling towers, chrome-plating, pigment, textile, and wood preservation, and the by-products cum effluents have resulted to pollution of the ecosystem [4]. Cr (VI) are toxic and are believed to

be carcinogenic, with effects on the circulatory system (Lung), kidney, nasal cavity, and the permissible limit of Cr (VI) in water is 0.05 (mg/L) while its concentration in industrial wastewater varies from 0.55 to 275 mg/L [5]. Hence, to remove deleterious heavy metals from the ecosystem, several methods have been used, which includes, chemical precipitation, co-precipitation, solvent extraction, coagulation, ion exchange, filtration, adsorption, evaporation, wet oxidation and membrane methods [6]. Adsorption have been utilised as a method of uptake of deleterious heavy metals using activated carbon, molecular sieve carbon, zeolites, nanoparticles and other composite adsorbents that have improved capacity for adsorption over a wide range of adsorbates, however, their high cost presents a great limitation to their application. Hence, there is an urgent need of utilization of materials that have low-cost and are abundant in nature yet possesses excellent properties for adsorption like the above-mentioned adsorbents [1]. The application of kaolin for adsorption is because of its low-cost, availability, abundance, shape-selective properties, and pore size which has made it an excellent material for adsorption. Kaolinite clay is considered as a good material for adsorption of deleterious metallic ions [4].

In this study, locally sourced clay was used as an adsorbent for the removal of Cr (VI) from industrial dye textile effluent. The study examined

adsorption conditions, which include contact time, temperature, and adsorbent dosage. And also the thermodynamics and kinetic of adsorption. The texture and morphology of the clay samples were obtained from X-ray diffraction (XRD), Brunauer Emmett and Teller (BET) and scanning electron microscope (SEM).

## 2. Experimental Procedure

### 2.1. Collection and pre-treatment of kaolinite clay

The kaolinite clay was obtained from Ahoko, Kogi State, Nigeria and sieved using 250  $\mu\text{m}$  mesh sieve. 300 g of the kaolinite clay was added into a 1000 mL beaker containing distilled water for 6 h. The organic particles left in the clay were removed using Moore and Reynolds technique of soil minerals purification. This method involves the treatment of the sample with small quantity of thirty percent hydrogen peroxide solution until all effervescence stopped [7]. The pre-treated kaolinite clay was allowed to stay overnight after which the supernatant was decanted. The slurry was oven dried at 373K. The kaolinite clay sample was characterized using XRD, BET, and SEM.

### 2.2. Chemical modification of clay sample

200 g of the kaolinite clay sample was added to 1.0 L of 0.50 mol/L of Potassium Dihydrogen Phosphate ( $\text{KH}_2\text{PO}_4$ ) and was thoroughly mixed with magnetic stirrer for 4 h at 300 rpm and later centrifuged for 20 min at 1000 rpm. The kaolinite was washed with distilled water to remove any trace of  $\text{PO}_4^{3-}$  ions and was dried at a temperature of 373.

### 2.3. Physicochemical characterization of the effluent

The dye effluent was collected from the discharge outlet of local dyer at Bosso, Niger State, Nigeria. The physicochemical analysis of the effluent was determined using standard methods [8] by the use of analytical grade chemicals. The heavy metal concentration of the effluent was determined using the Atomic Absorption Spectrophotometer (AAS).

### 2.4. Characterization of adsorbents

The X-ray diffraction (XRD) of the adsorbents was determined in a Randi-con MD 10 model. The pore properties and Brunauer, Emmett and Teller (BET) surface area of the adsorbents were determined from nitrogen adsorption-desorption isotherms in a micromeritics accelerated surface area and

porosimetry system 2010 model analyze, while scanning electron microscopy (SEM; Hitachi S4800) was used to examine the surface morphology of the adsorbents.

### 2.5. Adsorption studies of Cr (VI) ion

The adsorption experiment was performed using batch sorption technique at 298 K (25 °C) on a water bath shaker. The process was performed by adding 0.1 g of the unmodified and modified kaolinite clay to 50 mL of the effluent solution in a 100 mL pretreated plastic bottle. The effect of effluent contact time was studied by varying the contact time from 5.0 to 60.0 min. The influence of adsorbent dose and temperature were also studied under similar optimum experimental conditions at an effluent pH of 6.2, by varying the adsorbent dose from 0.1 to 0.5 g and temperature from 298 - 323 K, respectively.

The percentage of metallic ions removal at any time was evaluated using:

$$\text{Metal \%} = \frac{C_0 - C_t}{C_0} \times 100\% \quad (1)$$

where:  $C_0$  and  $C_t$  represent the initial concentration and at time  $t$  respectively (mg/l)

The quantity of adsorbates adsorbed by the kaolinite clay was calculated using equation (2),

$$q_t = \frac{(C_0 - C_t)V}{W(g)} \quad (2)$$

where:  $q_t$  is the amount of metallic ion removed at time  $t$  (mg/l),  $V$  is the quantity of adsorbate (l),  $W$  is the weight of the adsorbents used (g).

## 3. Results and discussion

### 3.1. Physicochemical characterization of dye effluent

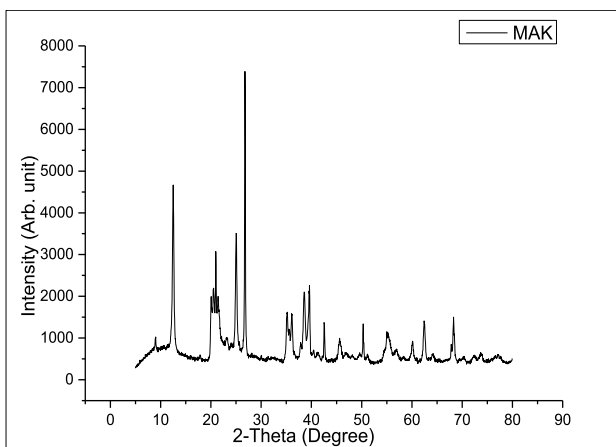
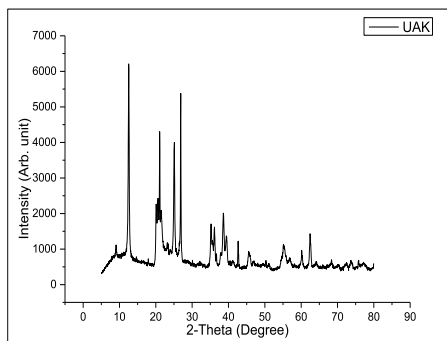
The properties of the raw effluent were determined using standard methods and the concentration of the heavy metals present in the effluent was determined using Atomic Absorption Spectrophotometer (AAS) as shown in Table 1.

### 3.2. Adsorbent Characterization

#### 3.2.1. XRD of unmodified and modified ahoko kaolinite clay

Fig. 1 shows the XRD spectra of the unmodified

and modified kaolinite clay. The XRD of the unmodified kaolin showed various peaks due to the presence of minerals in the clay. The unmodified clay shows well-defined reflections at  $2\theta$  values of 12.535, and 25.15, which are the typical characteristic peaks of kaolinite [9]. There were also considerable amounts of quartz detected at  $2(26.85)$  [10] with traces of feldspars. Fig. 1 showed that after modification there were shifts in the intensity of the peaks for the modified kaolinite clay. This suggests that the modification was only effective on the surface of the clay adsorbent [11]. The sharp and intense peaks and the presence of other weak peaks in the spectra indicate the amorphous nature of both adsorbents [12] and the amorphous nature of the Ahoko kaolinite clay suggests that Cr (VI) can easily penetrate its surface for efficient adsorption which is desirable for an effective removal [13].



**Fig.1.** XRD Spectra of the unmodified (UAK) and modified (MAK) clay sample

Parameter	Before Adsorption (mg/L)	After Adsorption (mg/L)
TDS	16281	1239.6
TSS	16.01	1,003
Copper	35.7	2.84
TH	20.28	10,857
Calcium	6.669	3.669
Zinc	15.8	6.91
Chromium	15.8	2.54
m	5.670	7.02
COD	734	297.83

### 3.2.2. SEM of unmodified and modified ahoko kaolinite clay

In Fig. 2 (a & b) the SEM micrographs surfaces of the modified and unmodified kaolin are presented and it reveals the presence of large particles that appeared to have been formed by several flaky particles stacked together in form of agglomerates. The unmodified and modified kaolin are made of variable clusters of different sizes with a prevalence of the particles in spherules. Some porosity is observed on the surface of the unmodified and modified kaolin which predict interesting adsorbent properties [13]. The SEM micrographs showed that the presence of pores, especially micro-pores which enhances the kaolin's capacity for adsorption of metals [14]. The analysis revealed that there was an increase in surface porosity with phosphate modification of the kaolin.

### 3.2.3. EDS of Modified and Unmodified Kaolinite Clay

The elemental composition of the modified and unmodified kaolin was determined with the EDS techniques. As shown in Fig. 3, the EDS spectral along with the elemental composition of the principal elements present in both kaolinite clay samples coupled with those with variable excitation energy. The peaks of the unmodified kaolin sample indicated that the kaolinite contain principally five elements namely Al, Si, Fe, K and O in varied energy, with Si and Al as the predominant constituents. The compositions of Al and Si for both modified and unmodified kaolin were close, though there was a slight decrease in the composition of Si with corresponding increase in Al and the disappearance of O after modification.

### 3.2.4. BET of unmodified and modified ahoko kaolinite clay

The treatment increased the specific surface area of the kaolinite clay to  $83.9 \text{ m}^2/\text{g}$ , as determined by the BET, which is desirable. The BET of unmodified clay ( $18.49 \text{ m}^2/\text{g}$ ) was close to the value ( $19.0 \text{ m}^2/\text{g}$ ) [15], whereas a lower SBET of  $7.65 \text{ m}^2/\text{g}$  was reported by Winda *et al.*, [16]. The factors that contribute to variation in the BET values of kaolinites include the type and purity of

the clay, the saturating cation, the out-gassing temperature and the general preparation of the sample. The increase in specific surface area and BET is attributed to an increase in pore property due to the etching reaction between silica and the phosphate [14]. An increase in the total pore volume and pore diameter from  $0.0153$  to  $0.0457 \text{ cm}^3/\text{g}$  and  $2.106$  to  $2.14 \text{ nm}$  respectively was obtained after modification.

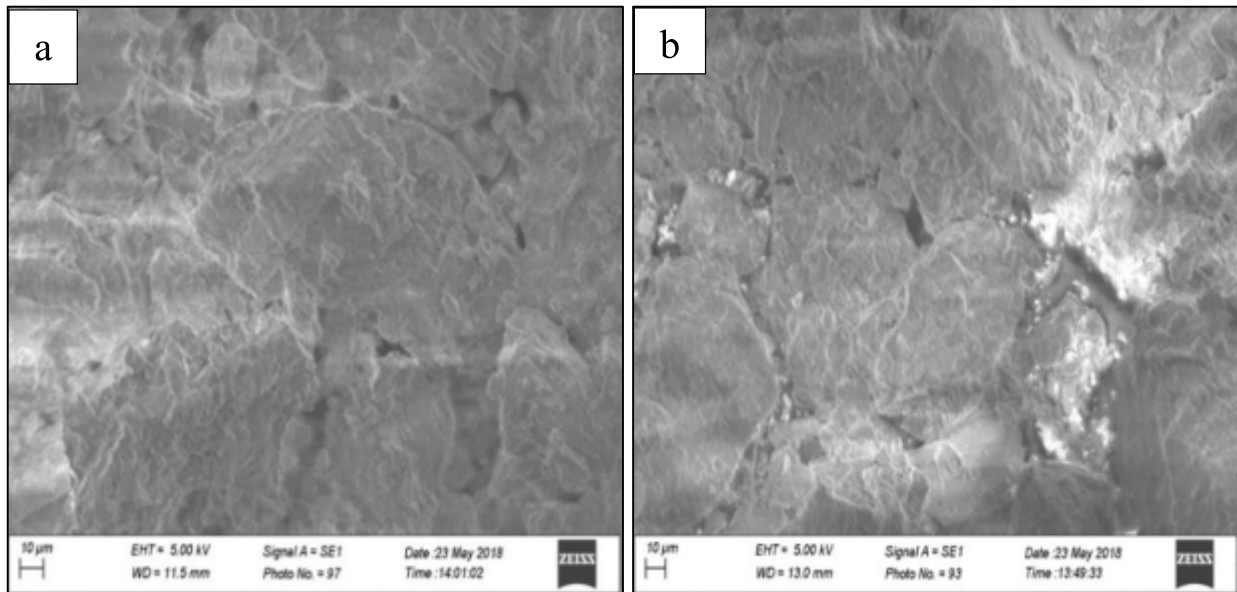


Fig. 2. SEM morphology of (A) unmodified and (B) modified kaolin

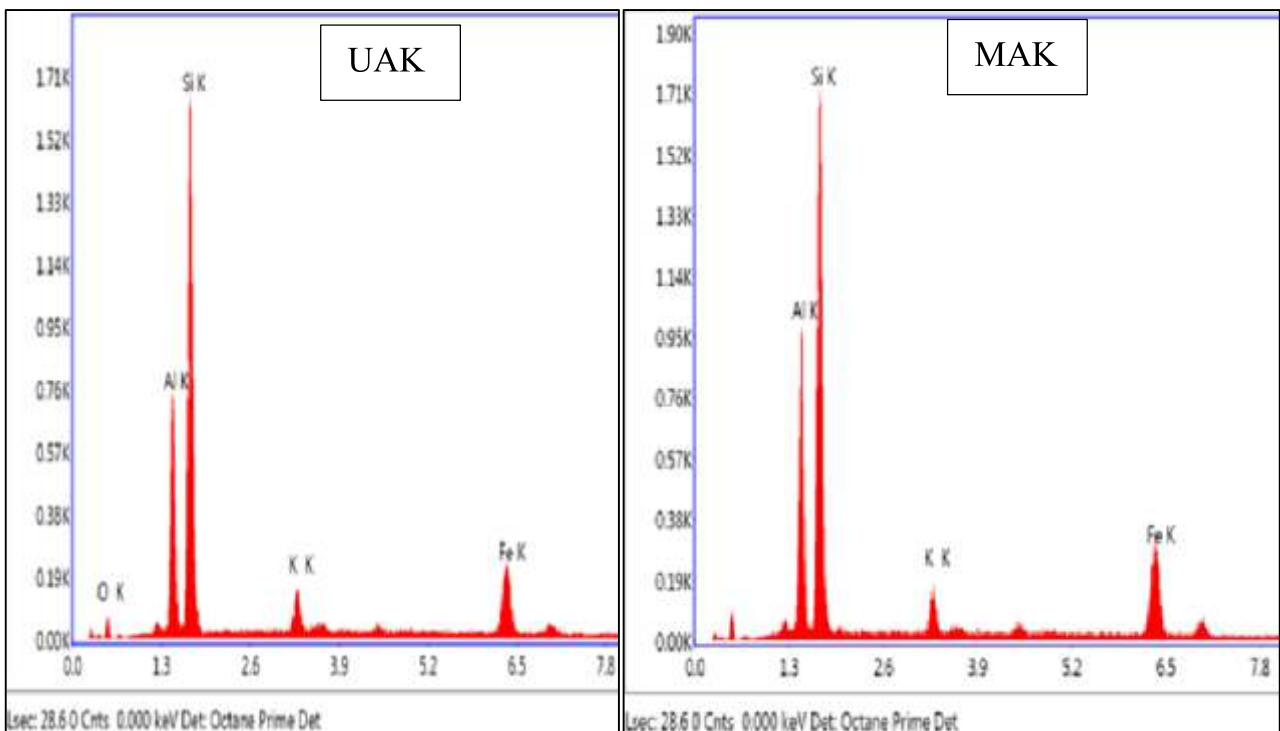


Fig. 3. EDS spectra of unmodified (UAK) and modified (MAK) Ahoko kaolinite

### 3.3. Adsorption mechanism

#### 3.3.1. Effects of contact time and initial concentration

The plots in Fig. 4 shows that the amount of the Cr (VI) ions adsorbed increases with contact time, until the equilibrium time was attained. The amounts of Cr (VI) ions adsorbed on both unmodified and modified Ahoko kaolinite clay sample in the first 5 min were observed to increase for both unmodified and modified Ahoko kaolinite clay samples, with higher adsorption on the phosphate-modified kaolinite clay. The higher adsorption by phosphate-modified clay may be due to its increased surface area and better cation exchange capacity as compared with unmodified clay [13], indicating the effectiveness of phosphate modification. The initial steep adsorption curve suggests that the adsorption occurs rapidly on the surface of the adsorbent, due to the presence of abundant active sites on the surface of adsorbents, which became saturated with time [17]. There was further increase in the amount of Cr (VI) ions adsorbed till the process attains equilibrium at contact time of 30 min for Cr (VI). Beyond which there was no significant increase in the sorption amount for Cr (VI) ions on both unmodified and modified Ahoko kaolinite clay samples. This is due to the accumulation of metal concentrations on the vacant sites, leading to decrease in gradient and adsorption rate, which results to longer diffusion

into the inner cavities in solutions [18]. Initially, sorption is controlled mainly by diffusion from the bulk to the surface of the clay, whereas, later, sorption is probably an attachment-controlled process due to the presence of fewer active sites [8].

#### 3.3.2. Effects of temperature on adsorption

The effect of temperature on Cr (VI) uptake using Ahoko kaolinite clay was performed varying two parameters namely: contact time (5, 10, 20, 30, 40, 50, and 60 min) and temperature (298, 303, 313 and 323 K) as shown in Fig. 5. The plots show that the percentage of adsorption of Cr (VI) increase with increased temperature till the temperature of 313 K where it attains a dynamic equilibrium. The increase could be the result of an increase in the mobility of the Cr (VI) cations with temperature. An increasing number of molecules could also acquire sufficient energy to undergo an interaction with active sites at the surface. Further increase in temperature will produce swelling effect within the internal structure of the kaolinite clay enabling large metal ions to penetrate further [19]. Also, kaolinite surface charge is a function of temperature, and surface charge becomes more negative with increasing temperature, so the affinity of the kaolinite surface for both metallic ions increased.

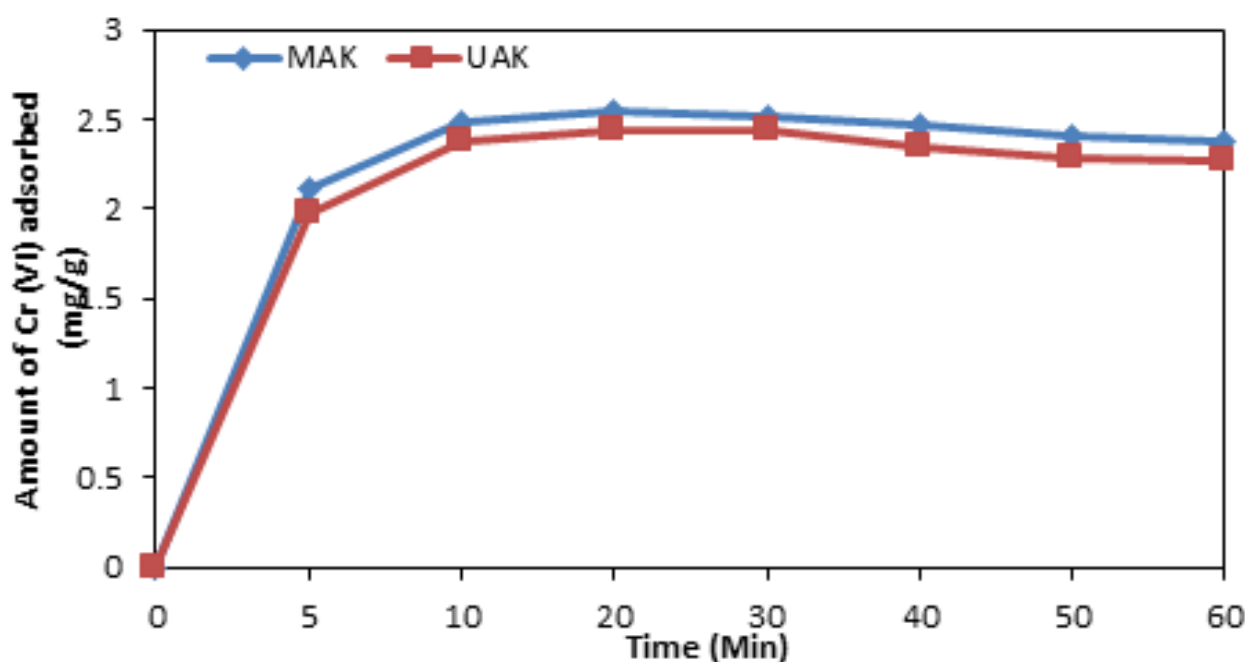


Fig. 4. Effect of contact time on adsorption of Cr (VI) onto unmodified and modified Ahoko kaolinite clay

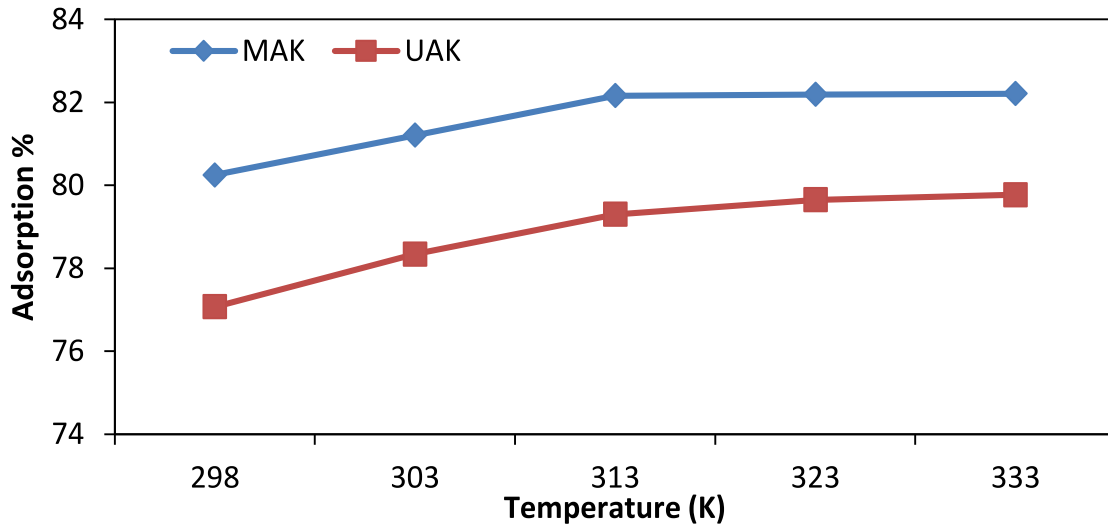


Fig. 5. Effect of temperature on Cr (VI) ion uptake onto unmodified and modified Ahoko kaolinite clay

### 3.4. Kinetic Study

Kinetic study of adsorption is imperative because adsorption rate and mechanism can be determined from it. After evaluating the equilibrium data, the results reveal that pseudo-first-order equation fitted very poorly to the data after the first 5.0 min, however, the pseudo-second-order showed an excellent fit for all adsorption time for both metallic ions onto unmodified and modified Ahoko kaolinite clay. The number of adsorbates adsorbed  $q_e$ , and pseudo-first and second order rate constant  $K_1$  and  $K_2$  were evaluated from the slope and intercept of the graphs in Fig. 6 and 7, are shown in Table 2. The validity of the order of sorption processes is based on two basic conditions, namely regression coefficient and calculated  $q_e$ . The pseudo-first rate constant  $K_1$  obtained for Cr (VI) and the  $q_e$  (cal) values obtained from the first-order-kinetic model did not agree with the experimental ( $q_e$  (exp)). This indicates that the adsorption of Cr (VI) onto both unmodified and modified Ahoko kaolin do not follow the first-order-kinetic model. The  $q_e$  (cal) values obtained from Pseudo second order were in agreement with the  $q_e$  (exp) values as seen in Table 2. Given that the correlation

coefficients for the second-order-kinetic model were very high ( $R^2 = 1.0000$ ). Thus, it is inferred that the adsorption process follows the pseudo-second order kinetic model [20].

### 3.5. Intra-particle diffusion

Intra-particle diffusion is the sole rate-determining step if the plot is linear and passes through the origin ( $C = 0$ ) as shown in Fig. 8 [21]. Table 2 indicates higher regression coefficient ( $R^2$ ) for both metal ions and the values of the intercept ( $C$ ) shows that the plots did not pass through the origin. This deviation from the origin is due to the difference in the rate of mass transfer in the initial and final stages of the adsorption process [22]. The presence of the boundary layer effect (Intercept,  $C$ ) showed the existence of the surface sorption indicating that intra-particle diffusion was not the only rate-limiting step [13]. Hence, the kinetics cannot be explained by intra-particle diffusion alone. This provides clear indication that although intra-particle diffusion is slow, it is not the slowest of the rate processes that determines the overall order. The interaction of metal ions with the clay surface remains the most significant rate process [4].

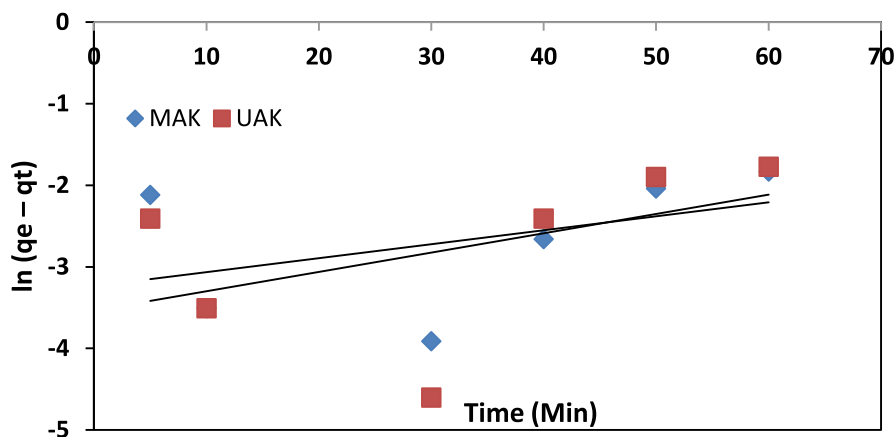


Fig. 6. Pseudo first-order kinetic plot for removal of Cr (VI) ion onto unmodified and modified Ahoko kaolinite clay at 298K

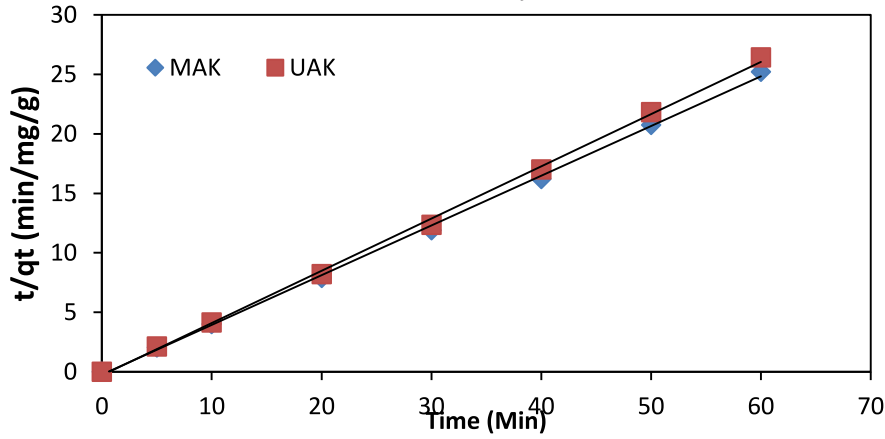


Fig. 7. Pseudo second-order kinetic plot for removal of Cr (VI) onto unmodified and modified Ahoko kaolinite clay at 298K

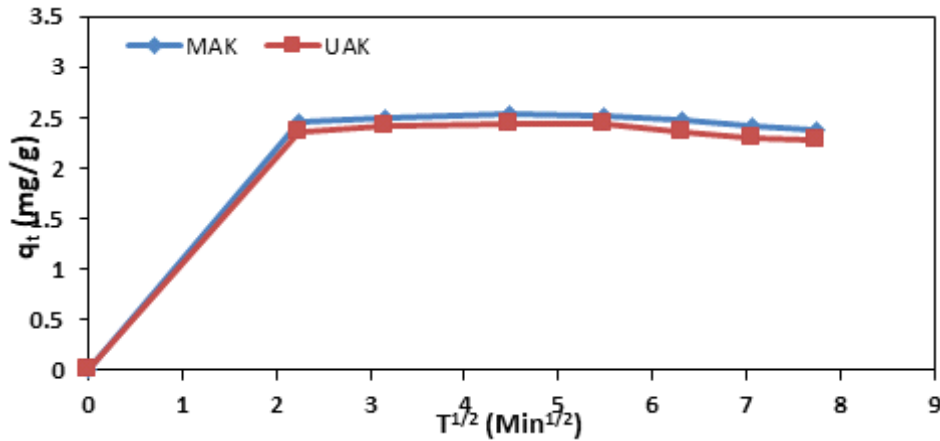


Fig. 8. Intra-particle diffusion plot for removal of Cr (VI) onto unmodified and modified Ahoko kaolinite clay at 298K

Table 2: Summary of kinetic parameters

	Cr (VI)	
	UAK	MAK
q <sub>e</sub> exp (mg/g)	2.44	2.54
Pseudo-First Order		
q <sub>e</sub> cal (mg/g)	0.00029	0.00058
K <sub>1</sub> (g/mg/min)	0.02373	0.01715
R <sup>2</sup>	0.22667	0.19269
Pseudo-Second Order		
q <sub>e</sub> cal (mg/g)	2.27751	2.39365
K <sub>2</sub> (g/mg/min)	0.6719	0.75804
R <sup>2</sup>	0.99885	0.99908
Intra-particle Diffusion		
K <sub>d</sub> (mg/g. min <sup>1/2</sup> )	0.2120	0.2237
C	1.1006	1.1384
R <sup>2</sup>	0.4443	0.4546

### 3.4. Adsorption isotherm

Equilibrium adsorption isotherms are used to relate the adsorbate concentration in solution and the amount on the adsorbent at equilibrium [14]. The isotherm studies as shown in Fig. 9, 10 and 11 were evaluated using Freundlich, Langmuir and Temkin isotherm at adsorbent weight of 0.1 g and 298 K. Langmuir model is a semi-empirical model to determine sorption rate and the degree of monolayer coverage of the adsorbates onto the adsorbent [23]. The Langmuir parameters  $K_L$  and  $q_m$  were calculated from the slope and intercept of the plots for Cr (VI) onto unmodified and modified kaolinite clay. The sorption capacity,  $q_m$ , which is a measure of the maximum sorption capacity corresponding to complete monolayer coverage showed that the kaolinite had a mass capacity for Cr (VI) (3.3241 mg/g) on modified kaolin in relation to Cr (VI) (3.1928 mg/g) on unmodified kaolin. The adsorption coefficient,  $K_L$  that is related to the apparent energy of sorption for Cr (VI) (0.2842 L/g) and on modified kaolin is greater in relation to the corresponding Cr (VI) (0.2683 L/g)

the unmodified kaolin. An essential feature of the Langmuir isotherm can be expressed in terms of a dimensionless separation factor ( $R_L$ ), defined as:

$$R_L = \frac{1}{1 + K_L C_0} \quad (3)$$

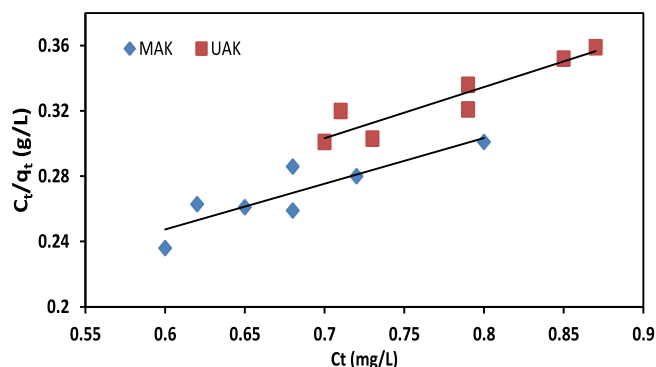
From the Langmuir constant, the values of  $R_L$  indicates the type of the isotherm to be either unfavorable sorption ( $R_L > 1$ ), linear sorption ( $R_L = 1$ ), favorable sorption ( $0 < R_L < 1$ ) or irreversible sorption ( $R_L = 0$ ). The  $R_L$  values for Cr (VI) (0.6901) on modified kaolin in relation to Cr (VI) (0.7023) on unmodified kaolin. The  $R_L$  values for metal ion adsorbed by both modified kaolinites are between 0 and 1, so the sorption process is favourable.

The Temkin isotherm is an isotherm model that explains uniformity in the sharing of the binding energies outlined by the sorption to the maximum binding energy  $q_T$  [23]. The Temkin parameters  $K_T$  and  $B$  were evaluated from the intercept and slope of the plots as shown in Table 3 for Cr (VI) onto unmodified and modified Ahoko kaolinite clay.

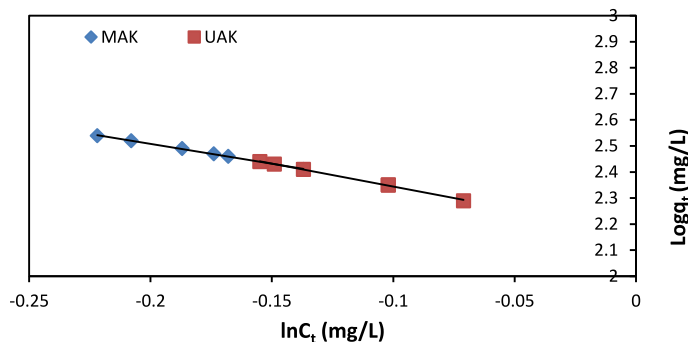
The Freundlich parameters  $K_F$  and  $1/n$  were evaluated from the intercept and slope of the plots as shown in Table 3 for Cr (VI) onto unmodified and modified kaolinite clay respectively. The Freundlich isotherm parameter  $\frac{1}{n}$  measures the adsorption intensity of metal ions on the kaolinite. The high  $1/n$  value of Cr (VI) (0.8972) on modified kaolin in relation to Cr (VI) (0.4894) on unmodified kaolin and the ultimate adsorption capacity  $K_F$ , of the adsorbent was calculated from the isothermal linear regression equation. The  $K_F$  value of Cr (VI) (2.6993 L/g) on modified kaolin is greater than that of Cr (VI) (2.5818 L/g) on unmodified kaolinite suggesting and confirming the effect of modification.

**Table 3:** Summary of isotherm model parameters

	Cr (VI)	
	UAK	MAK
Freundlich Isotherm		
1/n	0.4894	0.8972
$K_F$ (L/g)	2.5818	2.6993
$R^2$	0.9944	0.9979
Temkin Isotherm		
$B_T$ (mg/g)	-1.1682	-0.8043
$K_T$ (L/g)	0.2438	0.3004
$R^2$	0.9979	0.9770
Langmuir Isotherm		
$q_m$ (mg/g)	3.1928	3.3241
$K_L$ (L/g)	0.2683	0.2842
$R_L$	0.7023	0.6901
$R^2$	0.7821	0.8703



**Fig. 9.** Langmuir isotherm model for adsorption of Cr (VI) onto unmodified and modified Ahoko kaolinite clay



**Fig. 10.** Temkin isotherm model for adsorption of Cr (VI) onto unmodified and modified Ahoko kaolinite clay

### 3.5. Thermodynamics study

The mechanism of the sorption process was evaluated using thermodynamic properties such as Gibbs free energy change ( $\Delta G$ ), entropy change ( $\Delta S$ ), and enthalpy change ( $\Delta H$ ), which were evaluated using Van't Hoff equations to determine their values as shown in Table 4.



$$\Delta G = -RT \ln K_d \quad (4)$$

$$\Delta H = \Delta G + T\Delta S \quad (5)$$

Entropy change ( $\Delta S$ ), and enthalpy change ( $\Delta H$ ) were evaluated from the intercept, slope of the plots respectively and Van't Hoff equation was used to evaluate the Gibbs free energy. The negative values of free energy change ( $\Delta G$ ), suggests feasibility and spontaneity of the process. The positive values of  $\Delta S$  reveal increasing randomness at the solid–solution interface, while the positive values of enthalpy change ( $\Delta H$ ) suggest endothermic nature of the process, which explains the fact that adsorption efficiency increased with increase in temperature [24].

**Table 4:** Summary of thermodynamic parameters for unmodified and modified Ahoko kaolinite clay of Cr (VI)

T (K)	Cr (VI)	
	UAK	MAK
$\Delta H$ (J/mol)	1627.497	1167.697
$\Delta S$ (J/mol K)	16.091	15.494
T (K)	$\Delta G$ (J/mol)	
298	-3168.118	-3449.515
303	-3248.573	-3526.985
313	-3409.483	-3681.925
323	-3570.393	-3836.865
333	-3731.303	-3991.805

#### 4. Conclusion

The characterization of the clay sample indicates Ahoko kaolinite clay as a very good adsorbent for uptake of Cr (VI) ions from wastewater. SEM indicated an increase in the porosity of the  $H_2PO_4$ -modified adsorbent as compared with the unmodified form, which enhances metal ion adsorption on modified kaolinite clay. The BET indicate that modification increased the surface area and total pore volume of the kaolinite clay. The percentage adsorption increases for both adsorption of Cr (VI) ion onto unmodified and modified Ahoko kaolinite clay respectively, with increasing temperature (298 to 333 K) and adsorbent dosage (0.1 – 1.0 g), but the amount adsorbed per unit adsorbent weight decreased

significantly. The kinetic study reveals that the pseudo-first-order model reveals fit very poorly to the data after the first 5.0 min, however, the pseudo-second-order shown a good fit for all reaction time at different initial concentration.

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