

KINETIC AND THERMODYNAMIC STUDIES OF THE ADSORPTION OF Cu (II) AND Cr (VI) IONS FROM AN INDUSTRIAL EFFLUENT ON A KAOLINITE CLAY

Paul Egwuonwu Dim, Solomon Chukwunonso Olu, Joseph Onyebuchi Okafor

Department of Chemical Engineering
Federal University of Technology, Minna, Nigeria
E-mail: pevdim@yahoo.com

Received 18 February 2019
Accepted 20 December 2019

ABSTRACT

The present study indicates that Ahoko kaolinite clay is an effective adsorbent for the uptake of both Cu (II) and Cr (VI) ions from wastewater. The adsorption process is studied with variation of time, temperature and adsorbent dosage at an effluent pH of 6. X-ray diffraction (XRD), Fourier transforms infrared spectroscopy (FTIR), Brunauer Emmett and Teller (BET) and Scanning electron microscopy (SEM) are used to characterize the adsorbents. The XRD spectra show that the modification with KH_2PO_4 does not significantly change the crystal spacing of the clay mineral lattice structure; however, there are shifts in the intensity of the peaks for the modified kaolinite clay. The FTIR spectra show that certain functional groups are responsible for binding the metal ions from the solution. The SEM analysis indicates an increase of the porosity of the modified adsorbent as compared with that of the unmodified one enhancing the metal ion adsorption on the modified kaolinite clay. The BET study indicates that the phosphate modification increases the surface area and the total pore volume of the kaolinite clay. The kinetic study reveals that a pseudo-second order model shows a good fit in case of all reaction times and initial concentrations studied. The mechanism of the sorption process is evaluated using thermodynamic properties such as the enthalpy change (ΔH), the Gibbs free energy change (ΔG), and the entropy change (ΔS). The negative values of the free energy change (ΔG) suggest spontaneity and feasibility of the process. The positive values of the enthalpy change (ΔH) indicate an endothermic nature of the process. It is also noted that the Ahoko kaolinite clay has a higher affinity for adsorption of Cu (II) ions than that of Cr (VI) ions.

Keywords: thermodynamics, kinetics, adsorption mechanism, industrial effluent.

INTRODUCTION

The increased industrial and domestic activities arising from human population growth have caused more hazardous substances to be released into the environment within the past decades [1]. These result in a rising global concern about water pollution because of heavy deleterious metals and a great awareness in respect to the treatment of the industrial wastewater received from effluents discharge areas as it eventually returns to the water bodies. Many of the deleterious metal ions found in industrial wastewater, including those of cadmium, chromium, nickel, zinc, lead, and copper, result from various activities ranging from geological ones to batteries and paints production, leather tanning,

electroplating, metal coating, and metal finishing [2].

Chromium and copper find prevailing industrial applications as antifouling agents in cooling towers, chrome-plating, a production of pigments, fungicides, electric wires, roofing sheets, plumbing materials and textile, wood preservation, etc. The corresponding by-products and effluents pollute of the environment [3]. Cr (VI) and Cu (II) ions are toxic and are believed to be carcinogenic, with effects on the circulatory system, the lung, the kidney, the nasal cavity. The permissible limit of Cr (VI) ions in water is equal to 0.05 (mg/L), while the concentration in industrial wastewaters varies from 0.55 mg/L to 275 mg/L [4]. The permissible limit of Cu (II) ions in water suitable for drinking should be 1.3 mg/dm³ according to the Safe Drinking Water Act [5].

Adsorption has been used for removal of deleterious heavy metals using conventional adsorbents such as an activated carbon, which have been greatly utilised as excellent and effective adsorbents. But the high cost of the carbon production and its activation process has limited its use for wastewater treatment [6]. The application of kaolin as an adsorbent is determined by its low-cost, availability, abundance, shape-selective properties, and pore size. In fact, it is an excellent material for adsorption. This study is aimed to investigate the adsorption potential of the low cost Ahoko kaolin clay for the removal of Cu (II) and Cr (VI) species from textile industrial wastewater under some experimental conditions.

EXPERIMENTAL

Kaolinite clay collection and pre-treatment

The kaolinite clay was obtained from Ahoko, Kogi State, Nigeria and sieved using 250 μm mesh sieves. 300 g of the kaolinite clay were suspended in a 1000 ml beaker containing distilled water for 6 h, while the Moore and Reynolds technique of soil minerals purification was utilised to treat the kaolinite clay to remove any organic particles left. This method involved the treatment of the sample with small quantity of 30 % H_2O_2 solution until all effervescence stopped. The pre-treated kaolinite clay was allowed to stay overnight after which the supernatant was decanted. The slurry was oven dried at 373 K and the dried kaolinite clay sample was characterized using BET, FT-IR, XRD, and SEM/EDS.

Chemical modification of kaolinite clay

200 g of the kaolinite clay sample were added to 1.0 L of 0.50 mol/L of potassium dihydrogen phosphate (KH_2PO_4). The solution was thoroughly mixed with a magnetic stirrer for 4 h at 300 rpm and was then centrifuged for 20.0 min at 1000 rpm. The kaolinite was washed with distilled water to remove any traces of PO_4^{3-} ions, and dried at a temperature of 373 K.

Physicochemical characterization of the effluent

The dye effluent was collected from the discharge outlet of a local dyer at Kafanchan, Kaduna State, Nigeria. The physicochemical analysis of the effluent was determined by standard methods [7] using analytical grade chemicals. The heavy metal concentration of the effluent was determined by Atomic Absorption Spectrophotometry (AAS).

Characterization of the adsorbent

The X-ray diffraction (XRD) of the adsorbent was obtained by Randi-con MD 10 model and a Fourier-transform infrared spectrophotometer (Shimadzu 8400s) was used to identify the surface functional groups responsible for binding of Cu (II) and Cr (VI) ions and the effect of the phosphate modification. The pore properties and the Brunauer, Emmett and Teller (BET) surface area of the adsorbents were determined on the ground of nitrogen adsorption-desorption isotherms in a micromeritics accelerated surface area and porosimetry system 2010 model analyzer, while scanning electron microscopy (SEM; Hitachi S4800) was used to assess their morphology.

Adsorption studies of Cr (IV) and Cu (II) ion

The adsorption experiment was performed using a 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 the effluent contact time was studied by its variation. The influence of the adsorbent dose and the temperature was also studied under similar optimum experimental conditions at an effluent pH of 6.2 by varying their values.

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

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

where C_0 and C_t referred to the initial and the current concentrations (mg/l), respectively.

The quantity of the adsorbates was calculated using Eq. (2):

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

where q_t was the amount (mg/l) of the metallic ion removed at time t, V was the quantity of adsorbate (l), while W was the weight of the adsorbent used (g).

RESULTS AND DISCUSSION

Effluent and adsorbent characterization

The properties of the raw effluent are determined using standard methods [7] and the concentration of the heavy metals present in the effluent is evaluated by

Table 1. Dye effluent properties. XRD of unmodified and modified Ahoko kaolinite clay.

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
COD	5.670	7.02
BOD	734	297

TH = Total hardness

atomic absorption spectrophotometry (AAS) as shown in Table 1.

Fig. 1 illustrates the XRD spectra of the unmodified and modified kaolinite clay. The XRD of the unmodified kaolin shows various peaks due to the presence of minerals in the clay. The unmodified clay shows well-defined reflections at 2θ values of 12.535, and 25.15, which are the typical characteristic peaks of kaolinite [8]. There are also considerable amounts of quartz detected at 2θ

(26.85) [9] with traces of feldspars.

Fig. 1 shows that the modification with K_2PO_4 does not significantly change the crystal spacing of the clay lattice structure, as similar peaks to those of the unmodified kaolin are obtained. However, there are shifts in the intensity of the peaks of the modified kaolinite clay. This suggests that the modification with K_2PO_4 affects only the surface of the adsorbent but not the crystal lattice of the clay mineral [10].

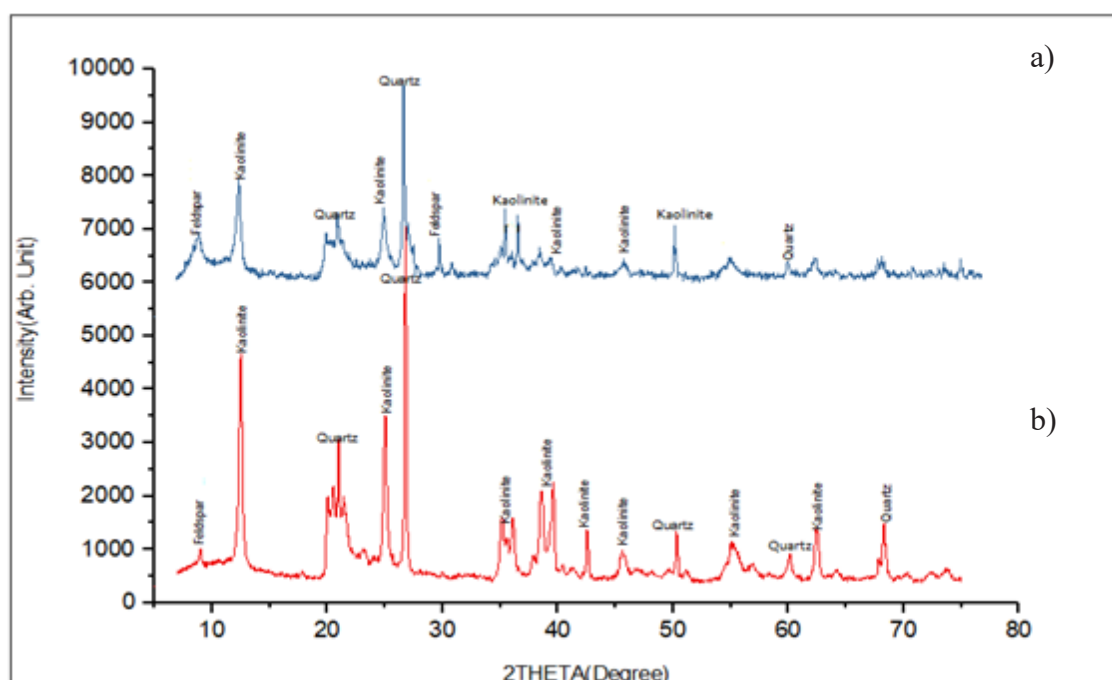


Fig. 1. XRD Spectra of the (A) unmodified and (B) modified kaolinite clay samples used.

The sharp and intense peaks as well as the presence of other weak peaks in the spectra indicate the amorphous nature of both adsorbents [11]. The amorphous nature of the Ahoko kaolinite clay suggests that Cr (VI) and Cu (II) ions can easily penetrate its surface which is desirable for their effective removal [12]

SEM/EDS of unmodified and modified Ahoko kaolinite clay

The SEM micrograph of the two kaolin samples studied are shown in Fig. 2 and 3. They reveal the presence of large particles that appear to have been formed by several flaky particles stacked together as agglomerates. The unmodified and modified kaolin samples are made of variable clusters of different sizes with a prevalence of spherule particles. Some porosity is observed on the surface of the unmodified and modified kaolin which predicts interesting adsorbent properties [12]. The SEM micrographs show the presence of pores, especially micro-pores, which enhances the kaolin's capacity for adsorption of metals [13]. The analysis reveals that there is an increase of the surface porosity as a result of the

phosphate modification. The EDS spectra along with the elemental composition of the unmodified and modified kaolin samples show the presence of the predominating elements coupled with those of variable excitation energy. The EDS peaks indicate that the kaolinite contains principally five elements, namely Al, Si, Fe, K and O in varied energy bands, with Si and Al as predominate constituents. The contents of Al and Si of both samples are close, though there is a slight decrease of Si content with a corresponding increase of that of Al and a disappearance of O after modification.

BET of unmodified and modified Ahoko kaolinite clay samples

The phosphate modification increases the specific surface area of the kaolinite clay, as determined by BET, which is desirable. The SBET of unmodified clay (18.49 m²/g) is close to the value (19.0 m²/g) reported in ref. [14], however, a lower SBET of 7.65 m²/g is found in ref. [15]. This may be due to the type and the purity of the clay, the saturating cation, the out-gassing temperature and the general preparation of the sample.

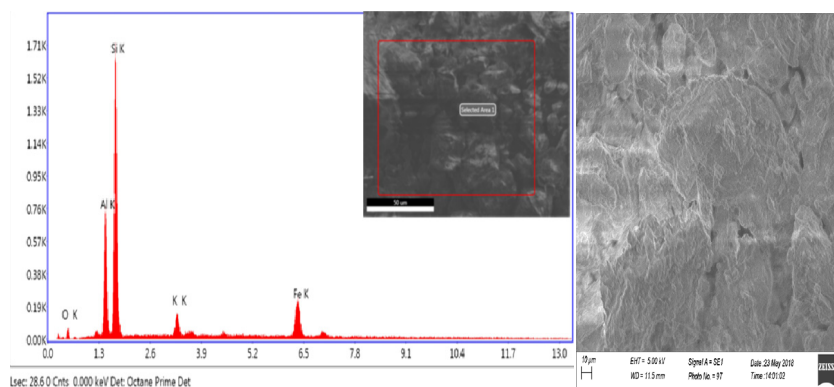


Fig. 2. SEM/EDS morphology of an unmodified kaolinite clay.

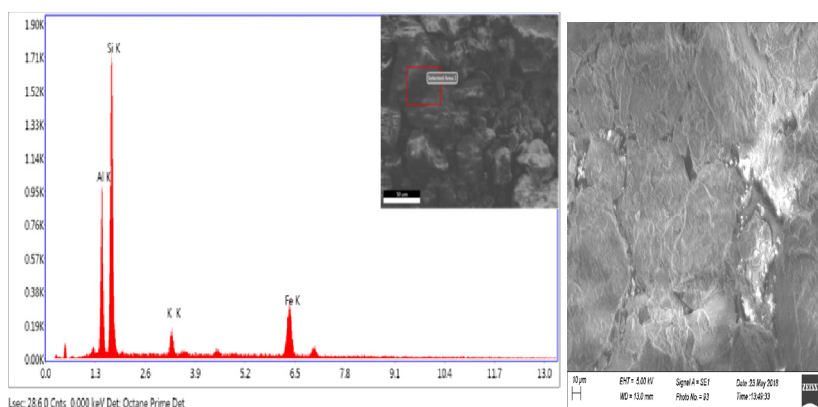


Fig. 3. SEM/EDS morphology of a modified kaolinite clay.

The increase of the specific surface area determined by BET is attributed to an increase of the pores' presence due to the etching reaction between the silica and the phosphate. An increase of the total pore volume and pore diameter from 0.0153 cm³/g to 0.0457 cm³/g and from 2.106 nm to 2.14 nm (21.06 Å to 21.4 Å), respectively, is obtained after the modification.

FTIR Spectra of the unmodified and modified Ahoko kaolinite clay samples

The FTIR spectra of the unmodified and phosphate-modified kaolinite clay samples are recorded to identify the surface functional groups responsible for binding Cu (II) and Cr (VI) ions and the phosphate modification effect. The unmodified clay (see Fig. 4(A)) shows absorption at 3904.05 cm⁻¹, 3695.73 cm⁻¹ and 3626.29 cm⁻¹, corresponding to the inner surface -OH stretching vibration of kaolinite. This verifies that the sample is rich in kaolinite [12]. The presence of outer surface -OH stretching is indicated by bands at 3410.26 cm⁻¹. An absorption band at 1635.69 cm⁻¹ is attributed to the OH bending vibration. It can also be assigned to the -COO- symmetric stretching vibration [16]. The presence of the outer surface OH and the symmetric COO- vibration

might suggest the presence of smectite in the kaolinite [17]. The Si-O bending vibration is outlined by bands at 995.3 cm⁻¹, while the stretching vibrations are observed at 779.27 cm⁻¹, 748.41 cm⁻¹, 678.97 cm⁻¹ and 64 cm⁻¹. The absorption bands at 910.43 cm⁻¹ correspond to Al-OH bending vibration.

All major OH-stretching bands have decreased intensities after the phosphate modification with some shift in the frequencies (see Fig. 4 (B)). The kaolinite phosphate modification of the adsorbent is indicated by the shift of the absorption bands from 3904.05 cm⁻¹ - 3626.29 cm⁻¹ to 3842.33 cm⁻¹-3255.95 cm⁻¹. The phosphate modified clay shows a new band of absorption at 2885.6 cm⁻¹ and 2638.71 cm⁻¹ corresponding to the OH stretching vibration, which is absent in the unmodified kaolin. This might indicate the presence of free OH sites on the modified kaolin. A similar result has been reported in ref. [18]. Similarly, a shift of OH bending from 1635.69 cm⁻¹ to 1658.84 cm⁻¹-1519.95 cm⁻¹ clearly indicates the involvement of OH group as an active site for binding of positively charged cations [18] and Si-O bending from 995.3 cm⁻¹ to 1010.73 cm⁻¹. These shifts of the absorption show the use of Si-O and Al-O-Si groups in the adsorption of the metal ions from the solution.

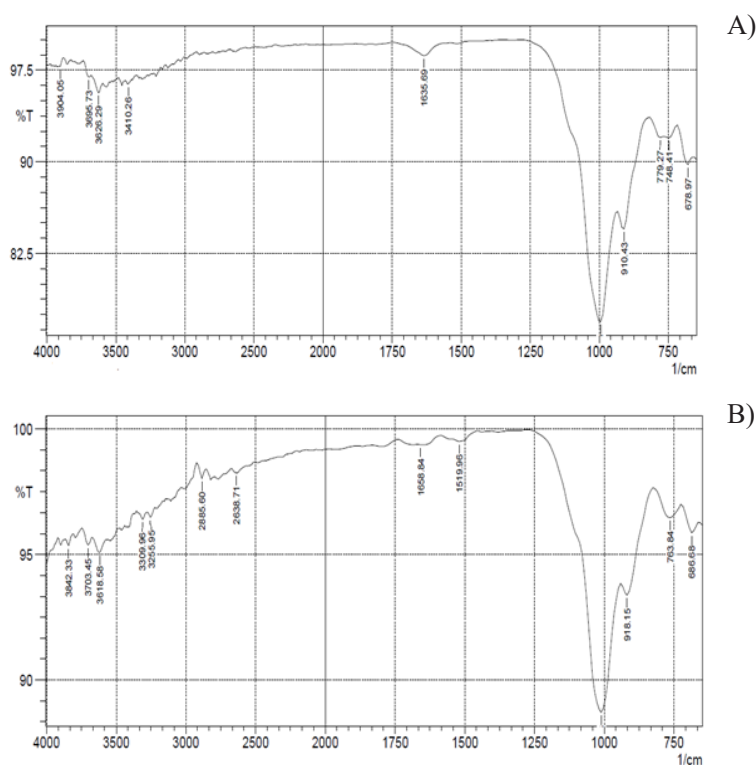


Fig. 4. FTIR Spectra of (A) unmodified and (B) modified kaolin.

Adsorption Mechanism

Effects of contact time

The graphs presented in Fig. 5 show that the amount of Cu (II) and Cr (VI) ions adsorbed increases with the contact time increase until the equilibrium time is attained. There is rapid adsorption of Cu (II) and Cr (VI) ions on the modified and the unmodified kaolin during the first 5 min. The adsorption on the modified sample is greater. The latter fact may be due to its increased surface area and better cation exchange capacity when compared with those of the unmodified clay [12]. This in turn indicates the effectiveness of the 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, which become saturated with time [19]. There is a further increase of the amount of Cu (II) and Cr (VI) ions adsorbed till the process attains equilibrium at a contact time of 30 min. There is no further significant increase of the sorbed amount of Cr (VI) and Cu (II) ions on both samples studied. This is due to the adsorbate accumulation on the vacant sites leading to a decrease of the gradient and the adsorption rate. This results in longer diffusion to the inner cavities of the adsorbent [12]. Initially, the sorption is controlled mainly by diffusion from the bulk to the surface of the clay, whereas later, the sorption becomes slow due to the presence of fewer active sites [7].

The rate of the metal ions adsorption on both adsorbents is observed to be greater in case of Cr (VI) when compared to that of Cu (II) ions. This could be attributed to the difference in their valence and ionic radii. The ionic radii of Cu^{2+} and Cr^{6+} refer to 0.73 \AA and 0.44 \AA , correspondingly [20]. It is evident that the ionic radii of

Cr (VI) ion are smaller than those of Cu (II) ion, which in turn facilitates the adsorption proceeding.

Temperature effect on the adsorption

The plots (Fig. 6) show that the percentage of Cr (VI) and Cu (II) ions adsorbed increases with the increase of the temperature till a value of 313 K is reached. The latter corresponds to that of the corresponding dynamic equilibrium. The increase could result from the increase of the mobility of the Cu (II) and Cr (VI) cations with the temperature increase. An increasing number of molecules could also acquire sufficient energy to undergo an interaction with the active sites on the surface. A further increase of the temperature will produce a swelling effect within the internal structure of the kaolinite clay enabling large metal ions to penetrate further [5]. Besides, the kaolinite surface charge is also a function of the temperature. It becomes more negative with the temperature increase so the affinity of the kaolinite surface for both metal ions will be increased. Furthermore, the tendency of Cu (II) and Cr (VI) ions leaving the liquid phase increases with the temperature increase [21].

Effect of the adsorbent dosage

The influence of the kaolinite clay amount on the removal of the metal ions is significant as shown in Fig.7. The dependence of the amount of Cu (II) and Cr (VI) ions adsorbed on the different adsorbent (Ahoko kaolinite clay) dosage shows that the percentage of the metal ions' removal increases with the adsorbent dosage increase in case of unmodified and modified Ahoko kaolinite clay samples. This is mainly due to an increase

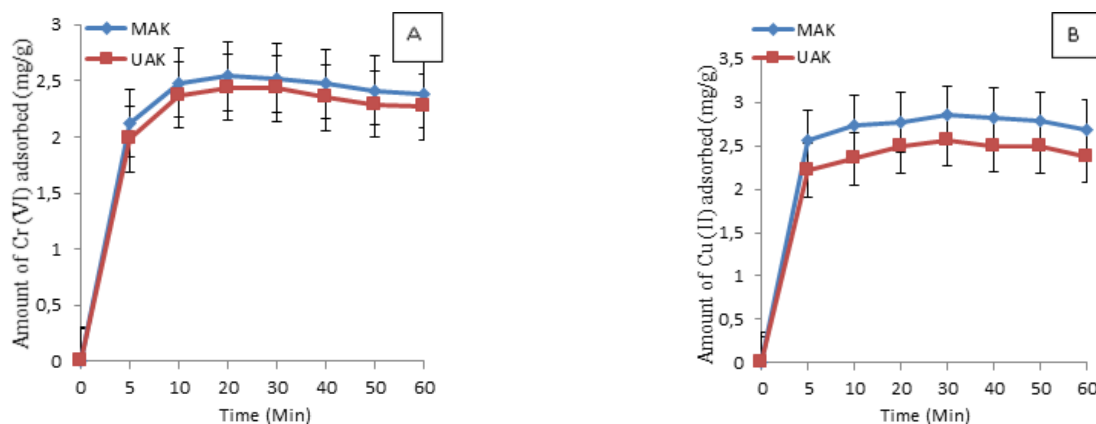


Fig. 5. A contact time effect on the adsorption of [A] Cr (VI) and [B] Cu (II) ions on unmodified and modified Ahoko kaolinite clay samples.

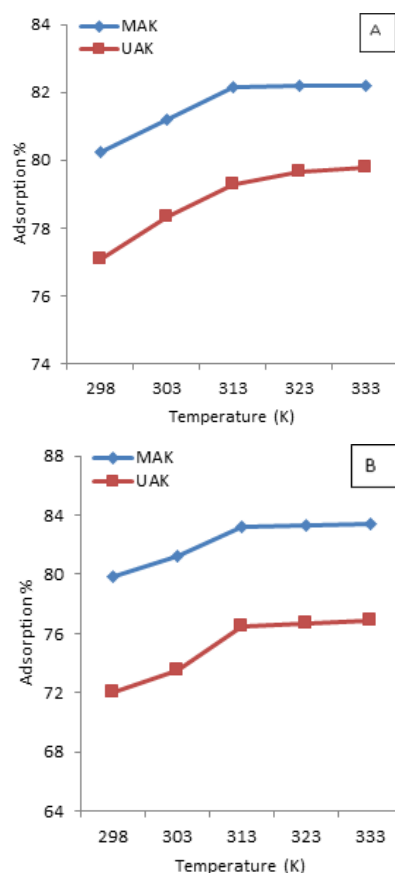


Fig. 6. A temperature effect on [A] Cr (VI) and [B] Cu (II) ion uptake by an unmodified (UAK) and a modified Ahoko kaolinite (MAK) clay sample at a constant time of 30 min (a dosage of 0.1 g and pH of 6.2).

of the adsorptive surface area and the availability of more active binding sites there [12]. However, the amount adsorbed per unit mass of the adsorbent decreases considerably with the increase of the dose of the adsorbent, which is basically due to adsorption sites remaining unsaturated during the adsorption reaction [22].

Kinetics studies

A study of the adsorption kinetics is imperative because it provides the determination of the adsorption rate and mechanism. The experimental results reveal that pseudo-first order equation cannot describe the data obtained within the first 5.0 min. But the pseudo-second order model shows an excellent fit in respect to all times tested for both metallic ions adsorbed on modified and unmodified Ahoko kaolinite clay samples. The amount of the adsorbate, q_c , and the pseudo-first and second order rate constant K_1 and K_2 , respectively, are evaluated

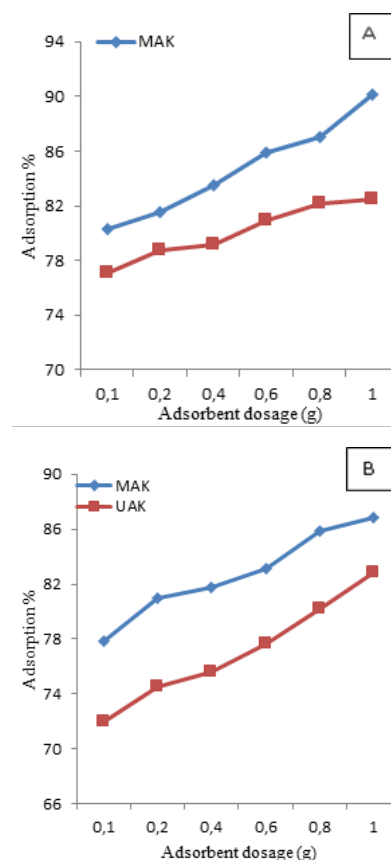


Fig. 7. An effect of the dosage on [A] Cr (VI) and [B] Cu (II) ions uptake by unmodified and modified Ahoko kaolinite clay samples.

from the slope and intercept of the corresponding graphs. The values obtained are shown in Table 2.

The validity of the sorption process order is based on two basic conditions referring to the regression coefficient and q_c [27]. The pseudo-first rate constant K_1 obtained for Cr (VI) and Cu (II) ions and the values of q_c (cal) obtained in correspondence with the first-order kinetic model do not agree with the experimental q_c (exp) values. This indicates that the adsorption of Cr (VI) and Cu (II) ions on both unmodified and modified Ahoko kaolin samples does not follow the model examined. The values of q_c (cal) values obtained following the pseudo- second order model agree with q_c (exp) values as seen from Table 2. Furthermore, the correlation coefficients referring to the second-order kinetic model are high ($R^2 = 1.0000$). Thus, it is inferred that the adsorption process studied follows the pseudo-second order kinetic model.

Intra-Particle Diffusion

The intra-particle diffusion is the sole rate-determining step if the corresponding plot is linear and passes through the origin ($C=0$) of the coordinate system used [24]. Table 2 shows high regression coefficient (R^2) values for both metal ions. The values of the intercept (C) indicate that the plots do not pass through the origin. This deviation is due to the different mass transfer rate in the initial and final stages of the adsorption process [12]. The presence of a boundary layer effect (Intercept, C) corresponds to the existence of surface sorption whose rate-limiting step is not entirely determined by intra-particle diffusion. This provides a clear indication that although the intra-particle diffusion is slow, it is not the slowest determining the overall process. The interaction of the metal ions with the clay surface remains the most significant rate process [3].

The study reported refers to the evaluation of the applicability of the Freundlich, Langmuir and Temkin isotherms in case of an adsorbent dosage of 0.1 g and 298 K. The Langmuir parameters K_L and q_m are calculated from the slope and the intercept of the corresponding linear plots obtained for Cu (II) and Cr (VI) ions adsorbed on modified and unmodified kaolinite clay. The sorption capacity, q_m , which is a measure of the maximum sorption capacity corresponding to a complete monolayer coverage is equal to 3.3241 mg/g and 3.2734 mg/g

in case Cr (VI) and Cu (II) ions on a modified kaolin sample, respectively, while the corresponding values obtained on the unmodified kaolin sample refer to 3.1928 mg/g and 2.8986 mg/g. The adsorption coefficient, K_L , related to the apparent energy of sorption amounts to 0.2842 L/g and 0.1989 L/g for Cr (VI) and Cu (II) ions adsorbed on a modified kaolin sample, respectively. The values pointed out are higher in respect to those obtained on an unmodified kaolin sample. They refer to 0.2683 L/g and 0.1935 L/g in case of Cr (VI) and Cu (II) ions, correspondingly. The data in Table 3 indicates further that, the effectiveness of kaolinite as an adsorbent corresponds to the relation Cr (VI) > Cu (II).

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

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

The values of R_L determine the type of the adsorption proceeding. It can be unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$). The R_L values obtained for Cr (VI) and Cu (VI) on a modified kaolin sample refer to 0.6901 and 0.5848, respectively. The corresponding values obtained in case of an unmodified kaolin one amount to 0.7023 and 0.5914, respectively. The R_L values for the metal ions adsorbed

Table 2. A summary of the kinetic parameters obtained. Adsorption isotherms

	Cr (VI)		Cu (II)	
	MAK	UAK	MAK	UAK
q_e exp (mg/g)	2.54	2.44	2.85	2.57
Pseudo-First Order				
q_e cal (mg/g)	0.00058	0.00029	0.16784	0.20815
K_1 (g/mg/min)	0.01715	0.02373	0.01531	0.01381
R^2	0.19269	0.22667	0.12186	0.21084
Pseudo-Second Order				
q_e cal (mg/g)	2.39365	2.27751	2.70946	2.5104
K_2 (g/mg/min)	0.75804	0.6719	0.9181	1.29412
R^2	0.99908	0.99885	0.99669	0.99939
Intra-particle Diffusion				
K_d (mg/g. min ^{1/2})	0.2237	0.2120	0.2715	0.2455
C	1.1384	1.1006	2.5815	2.2510
R^2	0.4546	0.4443	0.3321	0.3396

Table 3. A summary of the isotherm models parameters.

	Cr (VI)		Cu (II)	
	MAK	UAK	MAK	UAK
Freundlinch Isotherm				
1/n	0.8972	0.4894	0.5710	0.3306
K_F (L/g)	2.6993	2.5818	2.2137	2.1706
R^2	0.9979	0.9944	0.9980	0.9975
Temkin Isotherm				
B_T (mg/g)	-0.8043	-1.1682	-1.5565	-1.7985
K_T (L/g)	0.3004	0.2438	0.1101	0.0399
R^2	0.9770	0.9979	0.9988	0.9986
Langmuir Isotherm				
q_m (mg/g)	3.3241	3.1928	3.2734	2.8986
K_L (L/g)	0.2842	0.2683	0.1989	0.1935
R_L	0.6901	0.7023	0.5848	0.5914
R^2	0.8703	0.7821	0.7737	0.8621

by both types of kaolinite are between 0 and 1, which in turn indicates that the sorption process is favorable.

The Temkin isotherm is based on the uniformity of binding energies sharing [27]. The Temkin parameters K_T and B_T are evaluated from the intercept and the slope of the corresponding linear plots. The values obtained are listed in Table 3. The Temkin adsorption potential, K_T , of Cr (VI) (0.3004) and Cu (II) (0.1101) on a modified kaolin sample in relation to that of Cr (VI) (0.2438) and Cu (II) (0.0399) on an unmodified kaolin, indicates a lower kaolinite-metal ion potential of Cr (VI) ions adsorption due to their small ionic radii [19].

The Freundlich parameters K_F and $1/n$ are evaluated from the intercept and the slope of the corresponding linear plots. Their values are shown in Table 3. The Freundlich isotherm parameter $\frac{1}{n}$ measures the adsorption intensity of the metal ions on the kaolinite. The higher $1/n$ values of Cr (VI) (0.8972) and Cr (VI) (0.5710) ions on a modified kaolin in relation to those of Cr (VI) (0.4894) and Cu (II) (0.3306) ions on an unmodified kaolin indicate: (i) a preferential sorption

of Cr (VI) ions on a modified kaolin, probably due to their smaller ionic radii; (ii) an ability of the kaolinite to remove these metal ions from a solution; (iii) an effectiveness of the phosphate modification of Ahoko kaolinite clay [19]. The ultimate adsorption capacity, K_p , of the adsorbent is calculated from the isothermal linear regression equation. The values of K_F of Cr (VI) (2.6993 L/g) and Cu (II) (2.2137 L/g) ions on a modified kaolin are greater than those of Cr (VI) (2.5818 L/g) and Cu (II) (2.1706 L/g) ions, verifying that Cr (VI) ions have a greater adsorption tendency towards kaolinite than Cu (II) ions. This is due to the considerable difference between the ionic and hydrated radii of these metal ions [19].

Thermodynamics studies

The mechanism of the sorption process is evaluated on the ground of the values of the Gibbs free energy change (ΔG), the entropy change (ΔS), and the enthalpy change (ΔH). They are obtained using the Van't Hoff equation:

Table 4. Summarized thermodynamic parameters referring to the adsorption of Cr (VI) and Cu (II) ions on an unmodified and a modified Ahoko kaolinite clay.

T (K)	Cr (VI)		Cu (II)	
	UAK	MAK	UAK	MAK
ΔH (J/mol)	1627.497	1167.697	3006.079	2393.375
ΔS (J/mol K)	16.091	15.494	18.494	15.494
T (K)	ΔG (J/mol)		ΔG (J/mol)	
298	-3168.118	-3449.515	-2505.729	-2764.320
303	-3248.573	-3526.985	-2598.209	-2850.858
313	-3409.483	-3681.925	-2783.169	-3023.935
323	-3570.393	-3836.865	-2968.129	-3197.021
333	-3731.303	-3991.805	-3153.089	-3370.089

$$DG = -RT \ln K_d \quad (4)$$

and

$$DH = DG + TDS \quad (5)$$

The corresponding values as shown in Table 4. The negative values of the free energy change (ΔG) suggest feasibility and spontaneity of the process. The positive values of ΔS reveal an increasing randomness at the solid–solution interface [27], while the positive values of enthalpy change (ΔH) suggesting an endothermic nature of the process explain the fact that the adsorption efficiency increases with the temperature increase [28].

CONCLUSIONS

The characterization of the clay samples indicates that Ahoko kaolinite clay is a good adsorbent of Cu (II) and Cr (VI) ions from wastewater. The adsorption of Cu (II) ion and Cr (VI) ions increases with the temperature increase (298 K to 333 K) and that of the adsorbent dosage (0.1 g – 1.0 g), but the amount adsorbed per unit adsorbent weight decreases significantly. The kinetic study reveals that the pseudo-second order model provides a good fit in case of all reaction times and initial concentrations used as compared with the pseudo-first order one. The negative values of the free energy change (ΔG) suggest spontaneity and feasibility of the process. The positive values of the enthalpy change (ΔH) indicate an endothermic nature of the process.

REFERENCES

1. B. Saima, M.I. Muhammad Idrees, M. Al-Wabel, K. Ahmad, H. Hina, L. Ullah, Q.H. Cui, Sorption of Cr(III) from aqueous media via naturally functionalized microporous biochar: Mechanistic study, *Microchemical Journal*, 44, 2019, 242-253.
2. E.A. Omar, A.R. Neama, M.E. Maha, A study of the removal characteristics of heavy metals from wastewater by low-cost adsorbents, *Journal of Advanced Research*, 2016, 297-304.
3. A.S. Kovo, S.C. Olu, E. Afolabi, Kinetic and isotherm studies of adsorption of lead (II) ion onto functionalized Ahoko kaolin, *International Review of Chemical Engineering*, 6, 4, 2014, 1775-2035.
4. M.K. Rai, G. Shahi, V. Meena, R. Meena, S. Chakraborty, R.S. Singh, B.N. Rai, Removal of hexavalent chromium Cr (VI) using activated carbon prepared from mango kernel activated with H_3PO_4 , *Resource-Efficient Technologies*, 2, 2016, 63-70.
5. I. Mobasherpour, E. Salahi, H. Ebrahimi, Thermodynamics and kinetics of adsorption of Cu (II) from aqueous solutions onto multi-walled carbon nanotubes, *Journal of Saudi Chemical Society*, 18, 2014, 792-801.
6. I. Ali, M. Asim, T.A. Khan, Low cost adsorbents for the removal of organic pollutants from wastewater, *Journal of Environmental Management*, 113, 2012, 170-183.
7. K.G. Akpomie, F.A. Dawodu, Treatment of an automobile effluent from heavy metals contamination by an eco-friendly montmorillonite, *Journal of Advanced Research*, 6, 2015, 1003-1013.
8. A. Ksakas, A. Loqman, B. El Bali, B. Taleb, A. Kherbeche, The adsorption of Cr (VI) from aqueous solution by natural materials. *Journal of Material Environment Science*, 6, 2015, 2003-2012.
9. H.H. El-Maghrabi, S. Mikhail, Removal of heavy metals via adsorption using natural clay material, *Journal of Environment and Earth Science*, 4, 2014, 2224-3216.
10. E.I. Unuabonah, K.O. Adebawale, Optimization of kinetic data for two-stage batch adsorption of Pb (II) ions onto tripolyphosphate-modified kaolinite clay, *Journal of Chemical Technology and Biotechnology*, 84, 2009, 1726-173.
11. V.T.P. Vinod, R.B. Sashidhar, A. A. Sukumar, Competitive adsorption of toxic heavy metal contaminants by gumkondagogu: a natural hydrocolloid, *Colloid Surface B*, 75, 2010, 490-495.
12. K.G. Akpomie, A.F. Dawodu, Efficient abstraction of Ni (II) and Mn (II) ions from solution onto an alkaline-modified montmorillonite, *Journal of Taibah University for Science*, 8, 2014, 343-356.
13. M.A. Etoh, D.J.D. Dina, H.M. Ngomo, J.M. Ketcha, Adsorption of Pb(II) Ions on two clays: Smectite and kaolin the role of their textural and some physico-chemical properties, *International Journal of Applied Research*, 1, 2015, 793-803.
14. M.N. Timofeeva, N.P. Valentina, P.V. Konstantin, V.Z. Sergey, V.K. Victoria, G. Antonio, S.M. Oksana, A. Miguel, Effect of acid modification of kaolin and metakaolin on Brønsted acidity and catalytic properties in the synthesis of octahydro-2H-chromen-4-ol from vanillin and isopulegol, *Journal of Molecular*

- Catalysis A: Chemical, 414, 2016, 160-166.
15. R. Winda, F. Jean-François, U. Thamrin, M. Z'ephirin, Adsorption Characteristics of Bixin on Acid- and Alkali-Treated Kaolinite in Aprotic Solvents, *Bioinorganic Chemistry and Applications*, 1, 2018, 1-9.
 16. Y. Li, B. Xia, Q. Zhao, F. Liu, P. Zhang, Q.J. Du, Removal of copper ions from aqueous solution by calcium alginate immobilized kaolin, *Journal of Environmental Science*, 23, 2011, 404-411.
 17. G.E. Ekosse, Fourier transform infrared spectrophotometry and X-ray powder diffractometry as complementary techniques in characterizing clay size fraction of kaolin, *Journal of Applied Science Environment and Management*, 9, 2005, 43-48.
 18. K.G. Akpomie, F.A. Dawodu., Acid-modified montmorillonite for sorption of heavy metals from automobile effluent, *Beni-Suef University Journal of Basic and Applied Sciences*, 5, 2016, 1-12.
 19. A. Khansaa, K. Fawwaz, Sorption of Pb (II) Ions by Kaolinite Modified with Humic Acids, *Journal of Environmental Science and Engineering*, 5, 2016, 416-431.
 20. R.D. Shannon, Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides, *Acta Crystallization*, 32, 1976, 751-767.
 21. A. Khansaa, K. Fawwaz, Heavy Metals Adsorption from Aqueous Solutions onto Unmodified and Modified Jordanian Kaolinite Clay: Batch and Column Techniques, *American Journal of Applied Chemistry*. 6, 1, 2018, 25-34.
 22. J.T. Nwabanne, P.K. Igbokwe, Thermodynamic and kinetic behaviour of lead (II) adsorption on activated carbon derived from palmyra palm, *International Journal of Applied Science and Technology*, 2, 2012, 245-256.
 23. Z. Yaoyu, H. Yangzhuo, X. Yujia, M. Sijun, L. Xiaocheng, Y. Jiangfang, Y. Jian, Z. Jiachao, Q. Pufeng, L. Lin, Single and simultaneous adsorption of pefloxacin and Cu (II) ions from aqueous solutions by oxidized multiwalled carbon nanotubes, *Science of the Total Environment*, 646, 2019, 29-36.
 24. U.A. Guler, M. Sarioglu, Single and binary biosorption of Cu, Ni and methylene blue by raw and pretreated *Spirogyra* sp.: equilibrium and kinetic modelling, *Journal of Environment and Chemical Engineering*, 1, 2013, 269-377.
 25. N. Liu, W. Hang, W. Chih-Huang, H. Chi-Chin, Adsorption characteristics of Direct Red 23 azo dye onto powdered tourmaline, *Arabian Journal of Chemistry*, 11, 2018, 1281-1291.
 26. S.S. Ashish, M. M. Aniruddha, V.J. Vikas, A. A. Mansing, S.K. Sanjay, Removal of malachite green dye from aqueous solution with adsorption technique using *Limonia acidissima* shell as low-cost adsorbent, *Arabian Journal of Chemistry* 10, 2017, 3229-3238.
 27. L. Xiaojuan, W. Zhongmin, L. Haijun, N. Jingliang, L. Guiyin, Z. Zhide, Chitosan modification persimmon tannin bio adsorbent for highly efficient removal of Pb (II) from aqueous environment: the adsorption equilibrium, kinetics and thermodynamics, *Journal of Environmental Technology*, 40, 1, 2019, 12-23.
 28. D. Garmia, Z. Hassina, *Urtica dioica* leaves-calcium alginate as a natural, low cost and very effective bio adsorbent beads in elimination of dyes from aqueous medium: Equilibrium isotherms and thermodynamic studies, *International Journal of Biological Macromolecules*, 124, 1, 2019, 915-921.