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REMOVAL OF CU (II) FROM DYE EFFLUENT USING NATURAL AND PHOSPHATE-MODIFIED NIGERIAN KAOLINITE CLAY

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Abstract

This study indicates kaolinite clay as an effective adsorbent for the uptake of Cu (II) from wastewater. The adsorption process was studied with variation of time, temperature and adsorbent dosage at the effluent pH of 6. X-ray diffraction (XRD), Fourier transforms infrared spectroscopy (FTIR), Brunauer Emmett and Teller (BET) and Scanning electron microscopy (SEM) were used to characterize the adsorbents. XRD spectra showed that modification with KH2PO4 did not significantly change the crystal spacing on the lattice structure of the clay mineral; however, there were shifts in the intensity of the peaks for the modified kaolinite clay. The FTIR spectra showed that certain functional groups are responsible for binding the metal ions from solution. SEM indicated an increase in the porosity of the modified adsorbent as compared with the unmodified kaolinite, which enhances metal ion adsorption on modified kaolinite clay. The BET indicate that acid modification increased the surface area and total pore volume of the kaolinite clay. The kinetic study revealed that the pseudo-first-order model fitted poorly to the equilibrium data, however, the pseudo-second-order model had a good fit for all reaction time at different initial concentrations. The mechanism of the sorption process was evaluated using thermodynamic properties such as enthalpy change (ΔH), Gibbs free energy change (ΔG), and entropy change (ΔS), which were evaluated using Van't Hoff equations. The negative values of free energy change (ΔG), suggests spontaneity and feasibility of the process. The positive values of enthalpy change (ΔH) indicate endothermic nature of the process.

Keywords: Adsorption; Clay; Modification; Isotherms; Kinetics; Thermodynamics.

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1. Introduction

Increasing industrial and domestic activities arising from human population growth have caused more hazardous substances to be released into the environment within the past decades (Saima et al., 2019). There have resulted to rising global concern about water pollution because of heavy deleterious metals and great awareness on treatment of industrial wastewater that is received from effluents discharge areas because the wastewater eventually returns to the water bodies and land. Most of these metallic ions are contained in industrial wastewater, which includes cadmium, chromium, nickel, zinc, lead, and copper occurring in various industrial activities ranging from geological activities, batteries production, paints production, leather tanning, electroplating, metal coating, and metal finishing (Omar et al., 2016). Copper and its compounds lead to necrotic alteration in the liver and kidney, gastrointestinal irritation and lung cancer. The permissible limit of Cu (II) in water suitable for drinking should be 1.3 mg/dm3 according to the Safe Drinking Water Act (Mobasherpour et al., 2014). Adsorption has been used for removal of these heavy metal using conventional adsorbents such as activated carbon, which have been greatly utilized as excellent and effective adsorbent. Howbeit, the high cost of production of activated carbon and activation process has limited their applications for wastewater treatment (Ali et al., 2012). The application of kaolin for adsorption is because of its low-cost, availability, abundance, shape-selective properties, and pore size has made it an excellent material for adsorption (Kovo et al., 2014). The present study investigates the removal of copper (II) ion from industrial dye effluent using locally sourced kaolin clay

2. Materials and Methods

2.1. Pre-Treatment and Modification of Kaolinite Clay

The kaolinite clay was obtained from Ahoko, Kogi State, Nigeria and sieved using 250 µm mesh sieve. 200 g of the kaolinite clay was suspended into a 1000 ml beaker containing distilled water for 6 h. While Moore and Reynolds technique of soil mineral purification was utilised to treat the kaolinite clay to remove any organic particles left in the clay. 200 g of the kaolinite clay sample was added to 1.0 L of 0.50 mol/L of Potassium Dihydrogen Phosphate (KH2PO4) and was thoroughly mixed with magnetic stirrer for 4 h at 300 rpm and was later centrifuged for 20.0 min at 1000 rpm. The kaolinite was washed with distilled water to remove any trace of PO43- ions, and was dried at a temperature of 373 K and the dried kaolinite clay sample was characterized using BET, FTIR, XRD, and SEM/EDS.

2.2. Characterization of Adsorbents and Effluent

The X-ray diffraction (XRD) of the adsorbents was determined in a Randi-con MD 10 model and a Fourier-transform infrared spectrophotometer (FTIR; Shimadzu 8400s) was used to identify the surface functional groups responsible for binding of Cu (II) and the effect of phosphate modification. 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 analyser, while scanning electron microscopy (SEM; Hitachi S4800) was used to assess the morphology of the adsorbents.

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 using standard methods by the use of analytical grade chemicals. The heavy metal concentration of the effluent was determined by the use of the Atomic Absorption Spectrophotometer (AAS) (Akpome and Dawodu, 2015).

2.3. Batch Adsorption Study

The batch adsorption study was performed using batch sorption technique at 298 K (25 oC) inside 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 cleaned 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. The percentage of metallic ions removal at any time was evaluated using:

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

Where: Co and Ct represents the initial concentration and at time t respectively (mg/l)

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

$$qt = \frac{(\text{Co} - \text{Ct})\text{V}}{W(g)} \qquad (2)$$

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

3. Results and Discussions

The removal of copper (II) ion from dye effluent wastewater was carried out using raw and modified kaolin clay as an adsorbent.

3.1. Physicochemical Characterization of Dye Effluent

The physicochemical properties of the dye effluent were determined using standard methods (Akpome and Dawodu, 2015) and the concentration of the heavy metals present in the effluent was determined using Atomic Absorption Spectrophotometer (AAS) as shown in Table 1.

Table 1: Dye Effluent properties

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

3.2. XRD Of Unmodified and Modified Kaolinite Clay

The XRD spectra of the unmodified and modified kaolinite clay shown in Fig.1. 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 values of 12.535, and 25.15, which are the typical characteristic peaks of kaolinite (Ksakas et al., 2015). There were also considerable amounts of quartz detected at 2 (26.85) (El-Maghrabi and Mikhail, 2014) with traces of feldspars. Fig. 1 shows that modification with KH2PO4 did not significantly change the crystal spacing on the lattice structure of the clay mineral, as similar peaks to that of the unmodified kaolin were obtained. However, 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 and not on the crystal lattice of the clay mineral (Unuabonah and Adebowale, 2009). The sharp and intense peaks and the presence of other weak peaks in the spectra indicate the amorphous nature of both adsorbents (Vinod et al.,2010) and the amorphous nature of the kaolinite clay suggests that Cu (II) ion can easily penetrate its surface for efficient adsorption which is desirable for an effective removal (Akpome and Dawodu, 2014).

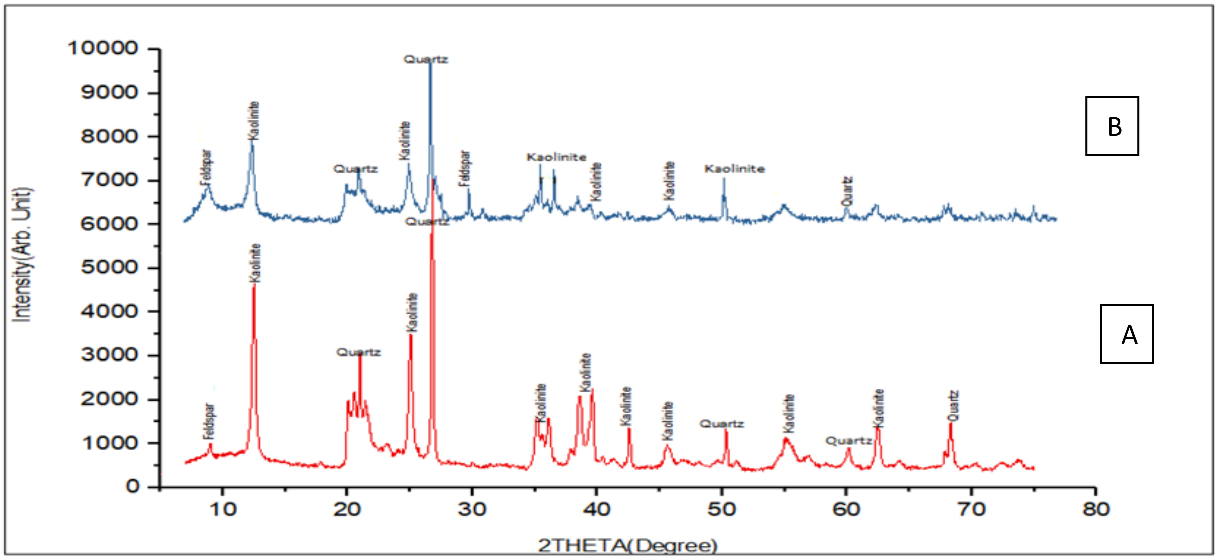


Figure 1: XRD spectra of (A) unmodified and (B) modified kaolinite clay samples

3.3. SEM of Unmodified and Modified Kaolinite Clay

The SEM micrograph in Fig. 2, are of the two studied kaolin present surfaces in the form of plates and 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 (Akpome and Dawodu, 2014). The SEM micrographs shows that the presence of pores, especially micro-pores enhance the kaolin's capacity for adsorption of metals (Etoh et al., 2015). The analysis revealed that there was an increase in surface porosity with phosphate modification of the kaolin.

3.4. BET of Unmodified and Modified Kaolinite Clay

The modification increased the specific surface area of the kaolinite clay, as determined by the BET and this is desirable. The BET of unmodified clay (18.49m2/g) was close to the value (19.0 m2/g) determined by (Timofeeva et al., 2016), whereas a lower BET of 7.65 m2/g was reported by (Winda et al.,2018). 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. An increase in the total pore volume and pore diameter from 0.0153 to 0.0457 (cm3/g) and 2.106 to 2.14 nm (21.06 to 21.4 Å) respectively was obtained after modification.

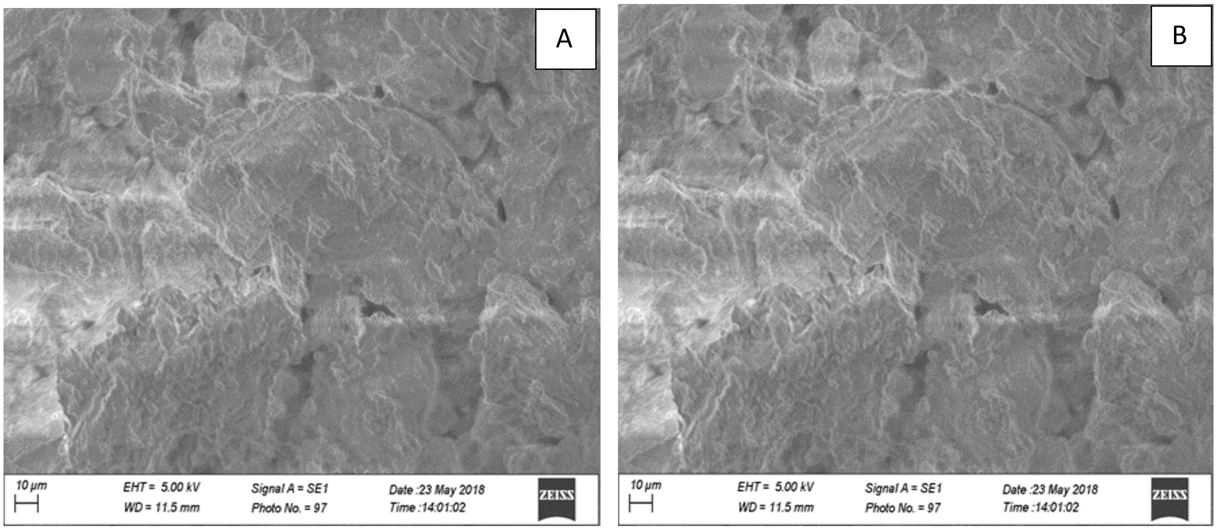
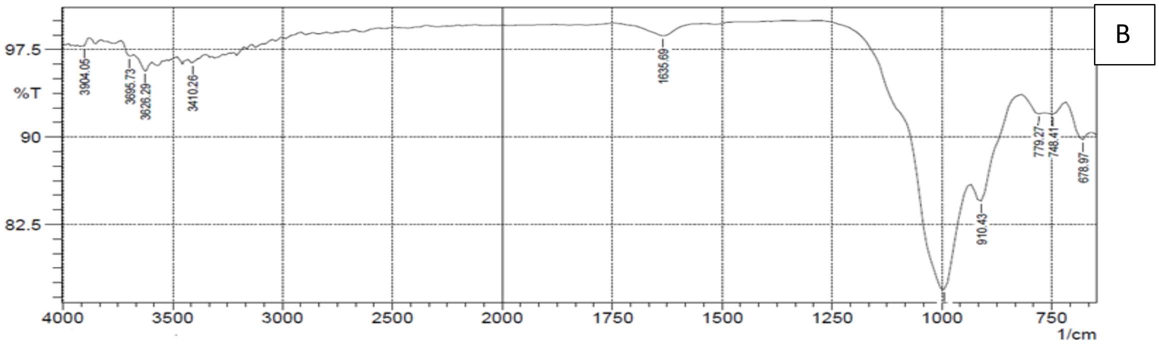


Figure 2: SEM morphology of (A) unmodified and (B) modified kaolinite clay

3.5. FTIR Spectra of Unmodified and Modified Kaolinite Clay

The FTIR spectra of unmodified and phosphate-modified kaolinite clay as shown in Fig. 3 were determined to identify the surface functional groups responsible for binding of Cu (II) and the effect of phosphate modification. The unmodified clay showed absorption at 3904.05, 3695.73 and 3626.29 cm−1, corresponding to the inner surface –OH stretching vibration of kaolinite, indicating the sample to be rich in kaolinite (Akpome and Dawodu, 2014). The presence of outer surface –OH stretching was indicated by bands at 3410.26 cm−1.



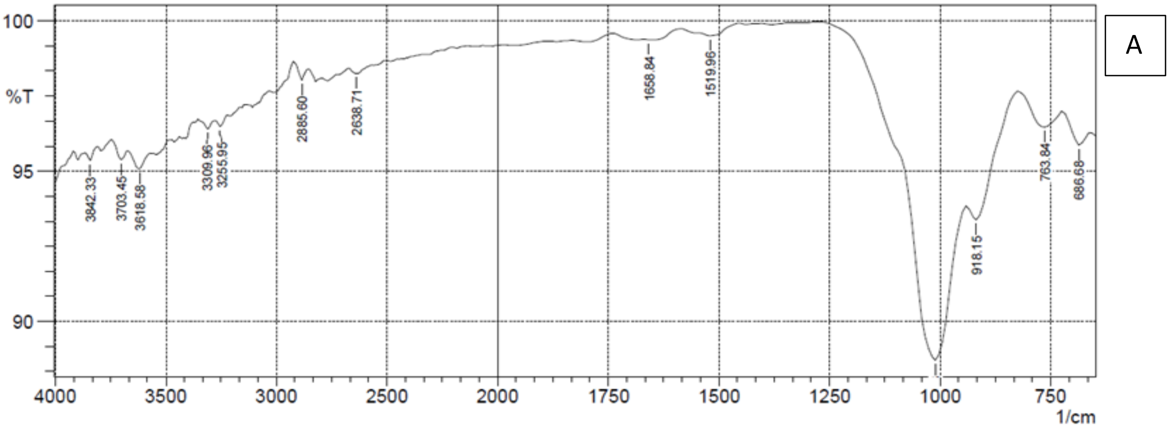


Figure 3: FTIR spectra of (A) unmodified and (B) modified kaolin

An absorption band at 1635.69 cm−1 represents the OH bending vibration and can also be assigned to the –COO– symmetric stretching vibration (Li et al., 2011). The presence of the outer surface OH and the symmetric COO− vibration might suggest the presence of smectite in the kaolinite (Ekosse, 2005). The Si–O bending vibration was represented by bands at 995.3 cm−1, while the stretching vibrations were observed at 779.27, 748.41, 678.97 and 64 cm−1. Absorption bands at 910.43 cm−1 correspond to the Al-OH bending vibration. All major OH-stretching bands have reduced intensities after phosphate modification with some amount of shift in the frequencies. Kaolinite phosphate modification of the adsorbent was indicated by the shift in absorption bands from 3904.05-3626.29 cm−1 to 3842.33-3255.95 cm−1, respectively. Phosphate modified clay showed a new band of absorption at 2885.6 and 2638.71 cm−1 corresponding to the OH stretching vibration, which was absent in the unmodified kaolin, this might indicate the presence of free OH sites on the modified kaolin. Similar result has been reported (Akpome and Dawodu, 2016). Similarly, a shift in the OH bending from 1635.69 to 1658.84-1519.93 cm−1 clearly indicated the involvement of the OH group as an active site for binding of positively charged cations (Akpome and Dawodu, 2016) and Si–O bending from 995.3 to 1010.73 cm−1. These shifts in absorptions showed the use of the Si-O and Al-O-Si groups in the adsorption of metal ions from solution.

3.6. Adsorption Mechanism

3.6.1. Effects of Contact Time and Initial Concentration

Figure 4 shows that the amount of the Cu (II) adsorbed increases with contact time, until the equilibrium time was attained. The amounts of Cu (II) adsorbed on both unmodified and modified kaolinite clay sample in the first 5 min were observed to increase for Cu (II) on both unmodified and modified 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 (Akpome and Dawodu, 2014), 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 become saturated with time (Khansaa and Fawwaz, 2016). There was further increase in the amount adsorbed of Cu (II) till the process attains equilibrium at contact time of 30 min for Cu (II). Beyond which there was no significant increase in the sorption for Cu (II) on both unmodified and modified kaolinite clay sample. 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 (Akpome and Dawodu, 2014). Initially, sorption is controlled mainly by diffusion from the bulk to the surface of the clay, whereas, later, sorption was probably an attachment-controlled process due to the presence of fewer active sites (Akpome and Dawodu, 2015).

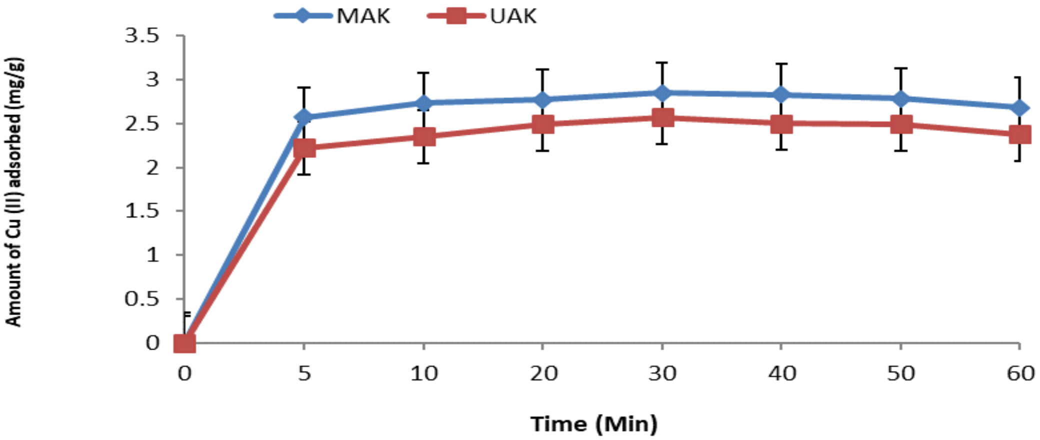


Figure 4: Effect of contact time on adsorption of Cu onto unmodified and modified kaolinite clay

3.6.2. Effects of Temperature on Adsorption

Figure 5 shows that the percentage of adsorption of Cu (II) ions increase with increased temperature till a temperature of 313 K was reached where it attained a dynamic equilibrium. The increase could be the result of an increase in the mobility of the Cu (II) 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 (Mobasherpour et al., 2014).

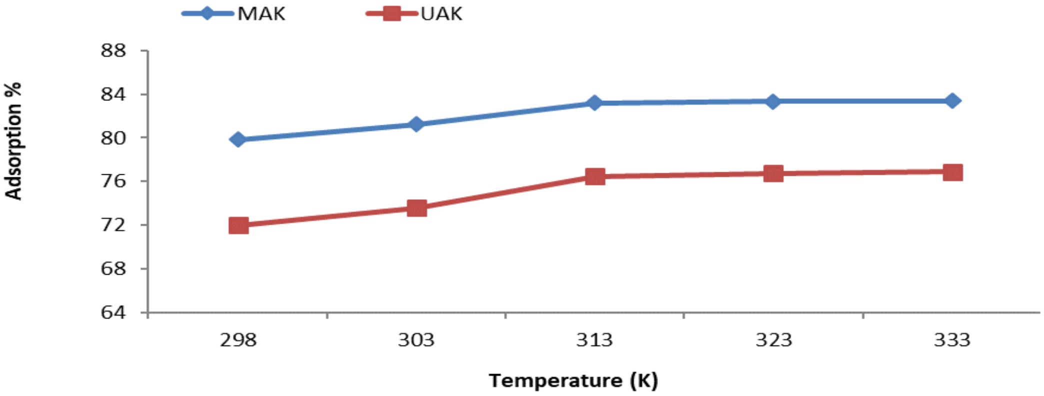


Figure 5: Effect of temperature on Cu (II) ion uptake onto unmodified and modified kaolinite clay

3.6.3. Effect of Adsorbent Dosage

The influence of the amount of kaolinite clay on removal of metallic ion is significant. The amount of Cu (II) adsorbed at different adsorbent (kaolinite clay) dosage as shown in Fig. 6, it can be observed that the percentage of the metallic ion removal increase with dosage of adsorbent. When the adsorbent loading is increased, the percentage of Cu (II) uptake increases significantly for both unmodified and modified kaolinite clay. This is mainly due to an increase in the adsorptive surface area and the availability of more active binding sites on the surface of the adsorbent with increase in adsorbent dose (Akpome and Dawodu, 2014). However, the amount adsorbed per unit mass of the adsorbent decreased considerably, the decrease in unit adsorption with increasing dose of adsorbent is basically due to adsorption sites remaining unsaturated during the adsorption reaction (Nwabanne and Igbokwe, 2012).

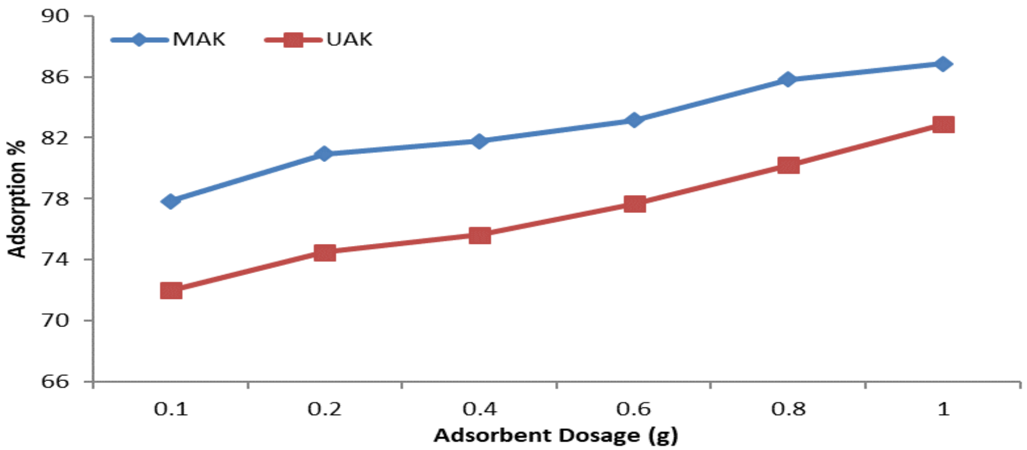


Figure 6: Effect of dosage on Cu (II) ion uptake onto unmodified and modified kaolinite clay

3.7. Kinetic Model

The equilibrium data results revealed that pseudo-first-order equation fitted very poorly to the data after the first 5.0 min (see Fig. 7), however, the pseudo-second-order showed an excellent fit for all adsorption time for Cu (II) ion onto unmodified and modified kaolinite clay (see Fig. 8). The pseudo-first rate constant K1 obtained for Cu (II) ions and the qe (cal) values obtained indicates that the adsorption of Cu (II) ion onto both unmodified and modified kaolin did not follow the first-order-kinetic model. The qe (cal) values obtained from Pseudo second order were in agreement with the qe(exp) values as seen in Table 2. given that the correlation coefficients for the second-order-kinetic model were very high (R2 = 1.0000). Thus, it is inferred that the adsorption process fitted for appropriately to the pseudo-second order kinetic model (Yaoyu et al., 2019). 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. 9 (Guler and Sarioglu, 2013). Table 3 indicate higher regression coefficient (R2) for both metal ions and the presence of the intercept (C), it 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 (Liu et al., 2018). 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 (Ashish et al., 2017);

hence, the kinetics cannot be explained by intra-particle diffusion alone. Thus, it is inferred that the adsorption process follows the pseudo-second order kinetic model.

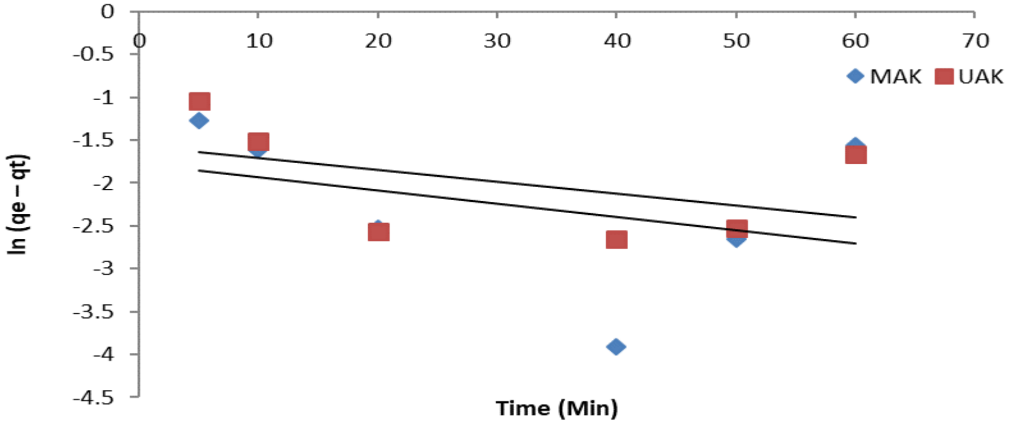


Figure 7: Pseudo first-order kinetic plot for removal of Cu (II) ion onto unmodified and modified kaolinite

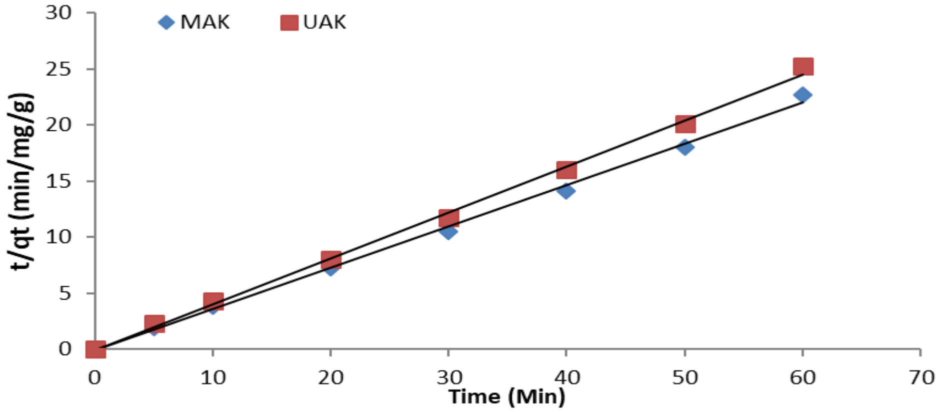


Figure 8: Pseudo second-order kinetic plot for removal of Cu (II) ion onto unmodified and modified kaolinite

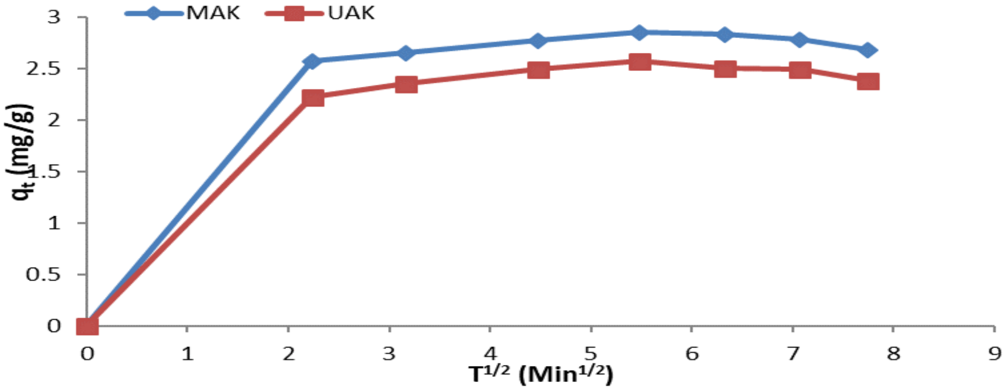


Figure 9: Intra-particle diffusion plot for removal of Cu (II) ion onto unmodified and modified kaolinite

Table 2: Summary of kinetic parameters

	Cu (II)	
	UAK	**MAK**
$q_e$exp (mg/g)	2.57	2.85
Pseudo-First Order		
$q_e$cal (mg/g)	0.20815	0.16784
K_1 (g/mg/min)	0.01381	0.01531
R^2	0.21084	0.12186
Pseudo-Second Order		
$q_e$cal (mg/g)	2.5104	2.70946
K_2 (g/mg/min)	1.29412	0.9181
R^2	0.99939	0.99669
Intra-particle Diffusion		
K_d(mg/g. min$^{1/2}$)	0.2455	0.2715
C	2.2510	2.5815
R^2	0.3396	0.3321

3.8. Thermodynamic Studies

The mechanism of the sorption process was evaluated using thermodynamic functions such as Gibbs free energy change (ΔG), entropy change (ΔS), and enthalpy change (ΔH), which were evaluated using Van’t Hoff equations to determine their values as shown in Table 3.

$$\Delta G = -RT \ln K_d \quad (3)$$
$$\Delta H = \Delta G + T\Delta S \quad (4)$$

Entropy change (ΔS), and enthalpy change (ΔH) 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 (ΔG), suggests feasibility and spontaneity of the process. The positive values of ΔS reveal increasing randomness at the solid–solution interface (Xiaojuan et al., 2019). while the positive values of enthalpy change (ΔH) suggest endothermic nature of the process, which supports the fact that adsorption efficiency in this case increased with increase in temperature (Garmia and Hassina, 2019).

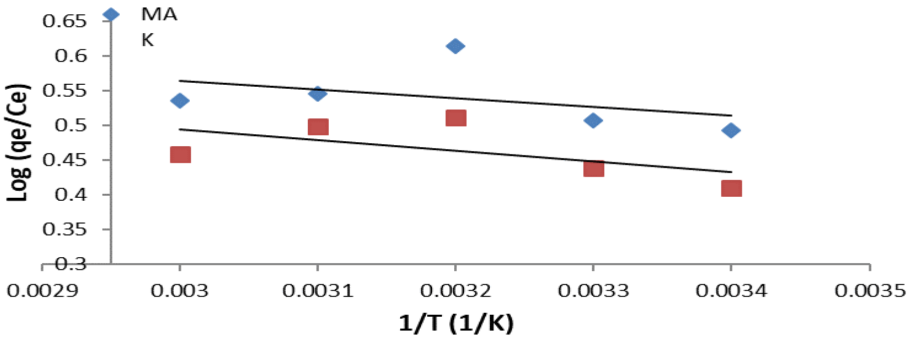


Figure 10: Relationship between 1/T and log (qe/Ce) for adsorption of Cu onto unmodified and modified kaolinite

Table 3: Summary of thermodynamic parameters for unmodified and modified kaolinite clay of Cu (II) ions

T (K)	**Cu (II)**	
	UAK	**MAK**
ΔH (J/mol)	3006.079	2393.375
ΔS (J/mol K)	18.494	15.494
T (K)	ΔG (J/mol)	
298	-2505.729	-2764.320
303	-2598.209	-2850.858
313	-2783.169	-3023.935
323	-2968.129	-3197.021
333	-3153.089	-3370.089

3.9. Adsorption Isotherm

The isotherm study was evaluated using Freundlich, Langmuir and Temkin isotherm at adsorbent weight of 0.1 g and 298 K.

3.9.1. Langmuir Isotherm Model

The Langmuir parameters KL and qm were evaluated from the slope and intercept of the plots for Cu (II) onto unmodified and modified kaolinite clay. The sorption capacity, qm, which is a measure of the maximum sorption capacity corresponding to complete monolayer coverage showed that the kaolinite had a mass capacity for Cu (II) (3.2734 mg/g) on modified kaolin in relation to Cu (II) (2.8986 mg/g) on unmodified kaolin. The adsorption coefficient, KL that is related to the apparent energy of sorption for Cu (II) (0.1989 L/g) on modified kaolin is greater in relation to the corresponding Cu (II) (0.1935 L/g) of the unmodified kaolin. An essential feature of the Langmuir isotherm can be expressed in terms of a dimensionless separation factor (RL), defined as:

$$RL = \frac{1}{[1 + K_L C_o]} \quad (5)$$

From the Langmuir constant, the values of RL indicates the type of the isotherm to be either unfavorable sorption (RL> 1), linear sorption (RL = 1), favourable sorption (0 < RL< 1) or irreversible sorption (RL = 0). The RL values for Cu (VI) (0.5848) on modified kaolin in relation to Cu (II) (0.5914) on unmodified kaolin. The RL values for metal ion adsorbed by both modified and unmodified kaolinite are between 0 and 1, so the sorption process is favourable.

3.9.2. Temkin Isotherm Model

The Temkin parameters KT and BT were evaluated from the intercept and slope of the plots of Cu (II) onto unmodified and modified kaolinite clay. The Temkin adsorption potential, KT, of Cu (II) (0.1101) on modified kaolin in relation to Cu (II) (0.0399) on unmodified kaolin.

3.9.3. Freundlich Isotherm Model

The Freundlich parameters KF and 1/n were also evaluated from the intercept and slope of the plots for Cu (II) onto unmodified and modified kaolinite clay respectively. The Freundlich isotherm parameter 1/n measures the adsorption intensity of metal ions on the kaolinite. The high 1/n value of (0.8972) on modified kaolin in relation to Cu (II) (0.3306) on unmodified kaolin, indicate the ability of the kaolinite to remove these metal ions from solution and the effectiveness of phosphate modification on kaolinite clay (Khansaa and Fawwaz, 2016). The ultimate adsorption capacity KF, of the adsorbent was calculated from the isothermal linear regression equation. The KF value of Cu (II) (2.2137 L/g) on modified kaolinite was greater than that of Cu (II) (2.1706 L/g) on unmodified, suggesting great affinity of Cu (II) onto modified kaolinite.

4. Conclusions

The percentage adsorption increases for adsorption of Cu (II) ion with increasing temperature and adsorbent dosage, but the amount adsorbed per unit adsorbent weight decreased significantly. The kinetic study reveals that the pseudo-second-order shown a good fit for all reaction time at different initial concentration as compared with the pseudo-first order model. The negative values of free energy change (ΔG), suggests spontaneity and feasibility of the process. The positive values of enthalpy change (ΔH) indicate the endothermic nature of the process. The kinetic study again revealed that the pseudo-first-order model fitted poorly, however, the pseudo-second-order model had a good fit for all reaction time at different initial concentrations. The equilibrium data were evaluated using Freundlich, Temkin, and Langmuir isotherm, with Freundlich have better fitting compared to others. The characterization of the clay sample indicates kaolinite clay as a very good adsorbent for uptake of Cu (II) from wastewater.

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