Adsorption study of Cu^{2+} ions from aqueous solution using kaolinite and metakaolinite

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ABSTRACT: *The adsorption potential of two samples of clays namely Kaolinite (KAO) and Metakaolinite (MKB) for the adsorption of Cu^{2+} ions from aqueous solution was investigated. The effects of pH, contact time, adsorbent dosage and initial concentration of Cu^{2+} ions solution were studied on the adsorption feasibility onto KAO and MKB. The maximum adsorption capacities of Cu^{2+} ions onto KAO and MKB were found to be 14.3 and 21.3 $mg.g^{-1}$ respectively .The Dubinin-Kaganer-Radushkevich model's revealed that, the Cu^{2+} ions adsorption onto KAO and MKB was governed by physical adsorption and the equilibrium study obeyed the Freundlich isotherm model. The kinetic investigation of Cu^{2+} ions adsorption onto KAO and MKB fitted well the pseudo-first-order kinetic model.*

KEYWORDS: *Adsorption, clays, isotherms, kinetics, wastewaters,*

I. INTRODUCTION

Due to their non-biodegradability and continual nature in wastewater, heavy metals have become a public health care. Their toxicity risk is still increased through accumulation in living organisms and following bioamplification in the food chain [1, 2]. Amongst heavy metals, Cu^{2+} ions are one of these widespread heavy metal ions to be followed up closely. It is well known that, Cu^{2+} ions is an essential metal in a the metabolism for some forms of life, thus, its accumulation in the human body causes some disorder such as brain skin, pancreas damage, heart diseases and central nervous system disorder. In the scientific literature, the Cu^{2+} ions are implicated in stomach and lung cancers due to its carcinogenic character, therefore, the World Health Organization (WHO), fixed the acceptable limit dose of Cu^{2+} ions in drinking water to 2.0 mg/L [3]. To limit its propagation, the adsorption of Cu^{2+} ions from wastewater is recommended before their rejection into the environment. To achieve this goal, the removal of Cu^{2+} ions from wastewater can be done using different techniques such as chemical coagulation, ion exchange, solvent extraction and adsorption. Among these above cited techniques, adsorption is the mostly appreciated due to its easier protocol, efficiency and low operation cost. And several adsorbents such as clays [4, 5] wheat shells [6], bagasse fly ash [7], modified goethite [8] and metakaolin-based geopolymer [9] have been successfully used for this purpose. A particular attention had been paid to clays which are available, cheaper and possessed interesting chemical and mechanical properties. Additionally, clay minerals have shown various adsorption capacities for heavy metal ions [10]. Several studies have been reported on kaolinite clay for adsorption of heavy metals from aqueous solutions [4, 11]. In this present work, a natural kaolinite (KAO) and its thermal treatment form, metakaolinite (MKB) were proposed as potential adsorbents for the removal of Cu^{2+} ions from aqueous solution.

II. MATERIALS AND METHODS

2.1 PREPARATION OF ADSORBENT AND ADSORBATE

The metal salt of $CuSO_4.5H_2O$ was obtained from Merck, Darmstadt, Germany and was of analytical grade. The kaolinite clay was collected in the locality of Kribi (South Region of Cameroon). Whereas, the metakaolinite (MKB) preparation from kaolinite was obtained by calcination in an electrical muffle furnace which was raised at the temperature of 700 °C with the heating rate of 5 °C/min for a residence time of 2 hrs. The muffle furnace was cooled to room temperature then the sample was collected and ground to retain particles size less than 90 μm sieves for further experiments.

2.2 BATCH ADSORPTION PROCEDURE

The Cu^{2+} ions stock solution of 1000 mg/L was prepared then diluted to obtain the required concentrations ranging from 200 to 800 mg/L. The initial pH value of solution was adjusted using 0.1 N of the solutions of NaOH and HCl. For the batch experiment, 25mL of the aqueous solution of copper (II) ions in a 100mL conical flask with optimum amount of adsorbent and initial Cu^{2+} ions concentration was fulfilled by shaking for the desired contact time. The content of the conical flask was centrifuged for 30 min and the copper (II) ions concentration of the filtrate was analyzed using UV-spectrophotometer. The amount of Cu^{2+} ions adsorbed per unit mass of adsorbent (Qe, mg/g) was calculated using the following formula.

$$Qe = \frac{(C_0 - Ce)}{m} xV \qquad (1)$$

where, C_0 and Ce (mg/g) are initial and equilibrium concentration of Cu^{2+} ions respectively,

V (L) is the volume of the solution and m(g) is the adsorbent mass.

2.3 ADSORPTION KINETICS

In order to understand the mechanism of Cu^{2+} ions adsorption on the adsorbents studied, four kinetics models that were, the pseudo first-order, pseudo second- order, Elovich and intra particle diffusion were considered to interpret the experimental data of the adsorption. The pseudo first-order kinetic model equation [12] is represented in an integral form as:

$$\ln (Q_e - Q_t) = \ln(Q_e) - K_1 t \qquad (2)$$

Where, Qe and Qt (mg/g) are the sorption capacities at equilibrium and at time t respectively, K_1 ($mg^{-1}min^{-1}$) is the rate constant of pseudo first-order kinetic model.

The pseudo second-order kinetic model [13] is expressed as:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \qquad (3)$$

Where, Qe and Qt (mg/g) are the sorption capacities at equilibrium and at time t respectively, k_2($g.mg^{-1}.min^{-1}$) is the rate constant of pseudo-second order kinetic model.

The Elovich equation [14] is generally expressed as:

$$\frac{dQ_t}{dt} = \alpha \exp(-\beta Q_t) \qquad (4)$$

Where, α ($mg^{-1}.g.min^{-1}$) is the initial sorption rate , β (g.mg-1) is the desorption constant during any one experiment. The integrated and simplified equation is given by:

$$Q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \qquad (5)$$

The intraparticle diffusion kinetic model [15] can be written in the linear form as:

$$\ln P = \ln k_{id} + a \ln t \qquad (6)$$

Where, P is the percent removal of copper (II) ions at time t, K_{id} is the intraparticular diffusion rate constant, a is a gradient whose value depends on the adsorption mechanism.

2.4 ADSORPTION ISOTHERMS

To evaluate the equilibrium adsorption data, three of the most widely used isotherms were chosen, namely the Freundlich, Dubinin-Kaganer-Raduskevich and Temkin isotherms. The general form of the Freundlich equation can be expressed by the Equation 7 as:

$$Qe = K_f C_e^{1/n} \qquad (7)$$

Its linearized form is given by:

$$\ln Q_e = \ln K_f + \frac{1}{n} \ln C_e \qquad (8)$$

Where, K_f (mg/g $(L/mg)^{1/n}$) and n are the Freundlich constants. The Dubinin-Kaganer-Raduskevich isotherm [16] is expressed by its linearized form Equation 9 below:

$$\ln Qe = \ln Q_{max} - \beta\varepsilon^2 \qquad (9)$$

Where, $\varepsilon = RT\ln\left(1 + \frac{1}{Ce}\right)$ is called the Polanyi Potential, Ea is the main energy of adsorption and gives information about the physical and chemical features of adsorption.

The Temkin isotherm is generally used in the linearized and rearranged form as Equation 10 and Equation 12 below:

$$Q_e = B \ln A + B \ln Ce \qquad (10)$$

Where, A (mg/L) is the equilibrium constant of binding corresponding to the maximum energy of binding, B (L/mg) is the constant related to the heat of adsorption. A plot of Qe versus ln Ce enables the determination of the isotherm constants A and B.

III.   RESULTS AND DISCUSSION

3.1   CHARACTERIZATION OF KAO AND MKB

The chemical composition of KAO and MKB adsorbents used in this study is summarized in Table 1. The analysis of Figure 1 clearly shows that the KAO sample is mainly composed of kaolinite mineral (K) as indicated from peaks existing at 2θ values of 12.46, 25, 31.56, 45.94 and 51.28 respectively. The XRD spectrum is matched with the JCPDS database file (PDF-01-089-6538). Whereas, the thermal treatment at 700 ^{o}C for 2 hrs decomposes the kaolinite structure into amorphous metakaolinite that has no diffraction patterns.

Table 1. The chemical composition of the KAO and MKB adsorbents used

Oxides (%)	KAO	MKB
SiO_2	47.10	59.6
CaO	0.21	0.15
Al_2O_3	33.90	34.4
Fe_2O_3	0.99	1.64
K_2O	0.42	0.44
Na_2O	< 0.10	< 0.1
MgO	0.20	0.17
TiO_2	0.83	1.46
F	< 0.01	< 0.01
SO_3	< 0.02	< 0.02
P_2O_5	0.034	0.056
L.i	14.75	2.10
Total	98.60	100.1

The FTIR spectroscopy analysis (Figure 2) shows a very strong and broad band at 3688-3620 cm^{-1} which corresponds to -OH stretching mode in the KAO [17]. The characteristic sharp band at 908 cm^{-1} can be assigned to the Al−O−H bending vibration of kaolinite. The bands at 1114, 1025 and 1000 cm^{-1} on KAO sample correspond respectively to bending vibration of Si-O, Si-O-Si and Si-O-Al. For the MKB sample, the last band appears at 1037 cm^{-1}. The transformation of kaolinite to metakaolinite can be proved by the disappearance of the band at 3688-3620 cm^{-1} on KAO sample which corresponds to the dehydroxylation of kaolinite and the presence of the band at 1698 cm^{-1} corresponds to the water molecules on the MKB sample owing to the hygroscopic property of metakaolinite after thermal treatment at 700 °C [18].

The BET measurements of surface area of the kaolinite and metakaolinite gave 20.1819 and 33.8331 m²/g, the pore volume of 0.0814 and 0.0935 cm^3/g for KAO and MKB respectively. It can be concluded that, the thermal treatment of kaolinite, conducted to an increase in surface area and the pore volume of the metakaolinite.
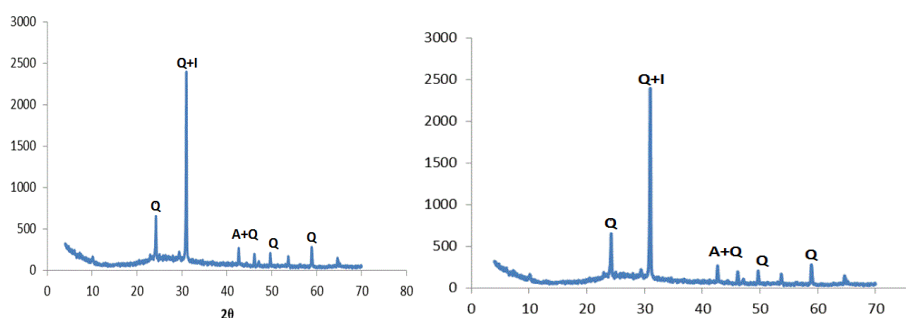

Figure 1. XRD Patterns of KAO and MKB
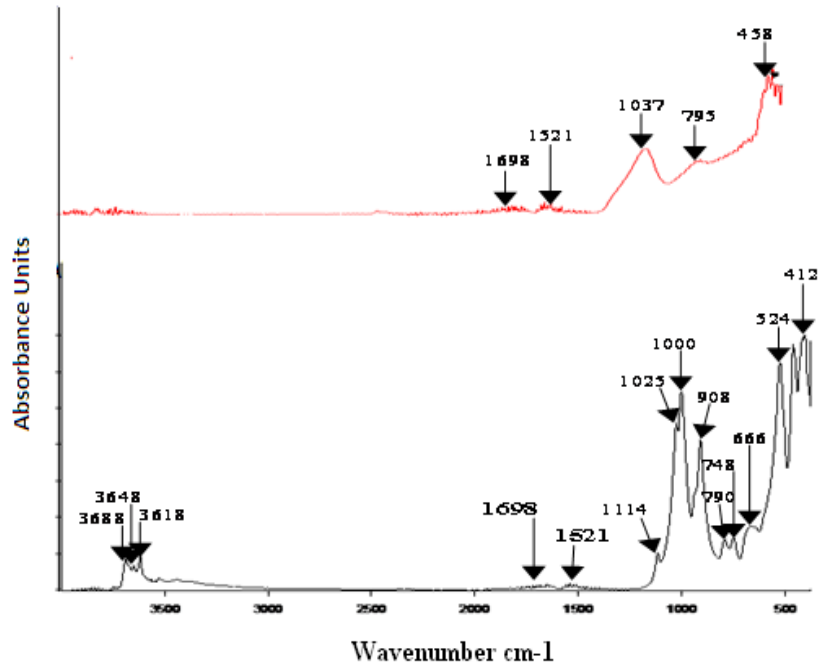
A=Anatase; I=illite; Q=quartz; K=Kaolinite; L=Lepidocrocite

Figure 2. FTIR spectra of KAO and MKB

3.2 BATCH ADSORPTION TESTS

3.2.1   EFFECT OF CONTACT TIME

The adsorption capacities of KAO and MKB were studied in the interval time of 10–150 min. The results obtained showed that the equilibrium is reached after a contact time of 90 min both for KAO and MKB. From the Figure 3, it can be seen that as the contact time increases the active sites on the two adsorbents were filled.
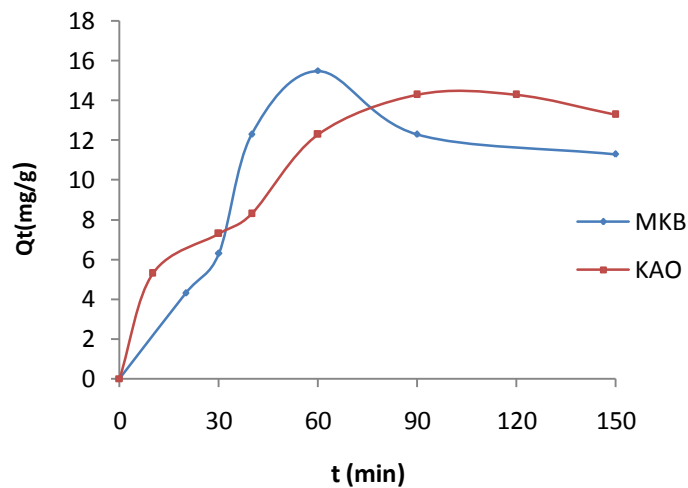

Figure 3. Effect of contact time on the adsorption of Cu^{2+} ions onto KAO and MKB

3.2.2   EFFECT OF ADSORBENT DOSE

The uptake of Cu^{2+} ions on KAO and MKB was found to decrease while the adsorbent dose increases (Figure 4). This can be explained by the fact that, as the amount of adsorbent increases, the total surface area available for the adsorption of Cu^{2+} ions reduces as a result of overlapping or aggregation of adsorption sites [19].
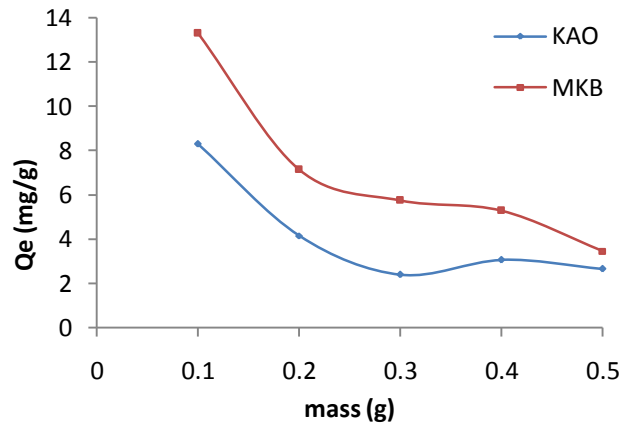

Figure 4. The effect of absorbent dose on the adsorption of Cu^{2+} ions on KAO and MKB

3.2.3   EFFECT OF pH

The pH of aqueous solution is important to control parameters in adsorption efficiency [20, 21]. The pH value of solution that changed with respect to the hydronium ions concentration influences the charges of sorbate and adsorbent. The initial pH values of solution were varied from 2 to 4. The Cu^{2+} ions adsorption efficiency of KAO and MKB are in the range of 30–50 % at strongly acidic conditions (Figure.5). This Incresing may be due to much more number of hydronium (H_3O^+) ions than the number of hydroxylated Cu^{2+} ions which result in a hard competition. Under such conditions, the clay surface interacts with water in an acidic medium forming complex ions [22]. The complex ions with positive charge considerably prevent Cu^{2+} ions approaching the clay mineral surface due to electrostatic repulsion and consequently the Cu^{2+} ions efficiency adsorption is reduced.
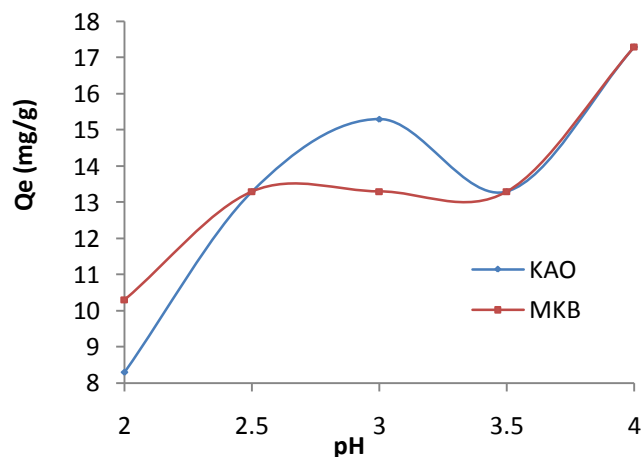

Figure 5. Effect of pH on Cu^{2+} ions adsorption on KAO and MKB

3.2.4   EFFECT OF INITIAL Cu^{2+} CONCENTRATION

The Cu^{2+} ions removal efficiency (Figure 6) showed that the amount of Cu^{2+} ions adsorbed increases with the increase in Cu^{2+} ions initial concentrations. This increase in Cu^{2+} ions concentration gradient was the driving force behind overcoming all mass transfer resistances of the copper, between the aqueous and solid phase. It also led to an increase in the equilibrium sorption, until sorbent saturation was achieved. Similar trend has been reported for adsorption capacity of tea ash, applied for fluoride removal [23].
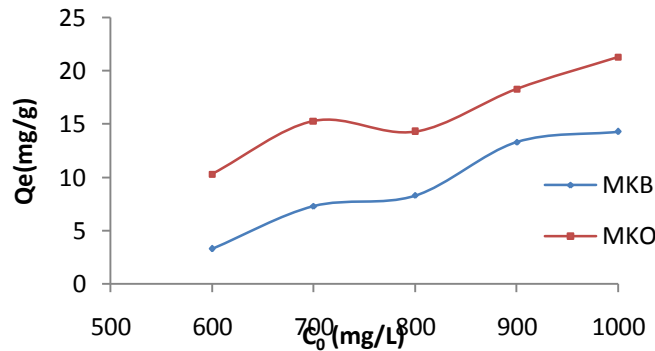

Figure 6. Effect of initial concentration on Cu^{2+} ions adsorption on KAO and MKB

3.2.5   ADSORPTION KINETICS STUDIES

The straight-line plots of the various kinetic models are presented on Figure 7, Figure 8, Figure 9 and Figure 10, while the parameters for these models are given in Table 2. The values of R^2 are closer to unity for the pseudo-first-order model compared to the pseudo-second-order, Elovich and intra particle diffusion models. Thus, the adsorption phenomenon of the Cu^{2+} ions adsorption on both materials followed the pseudo-first-order model during the entire period of adsorption. This result is in contradiction with those found by others authors who studied the removal of metal ions from aqueous solutions by natural geological materials [2, 4, 5, 14, 15].
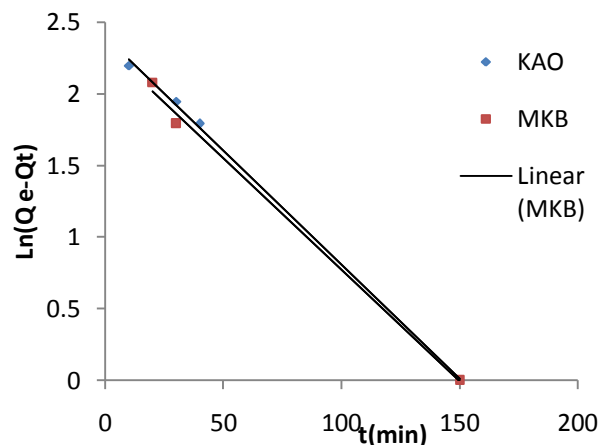

Figure 7. Pseudo first order model's plot on Cu^{2+} ions adsorption on KAO and MKB
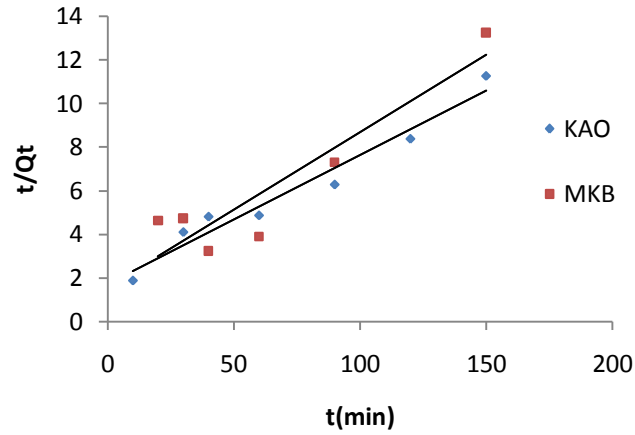
Figure 8. Pseudo second order model's plot on Cu^{2+} ions adsorption on KAO and MKB
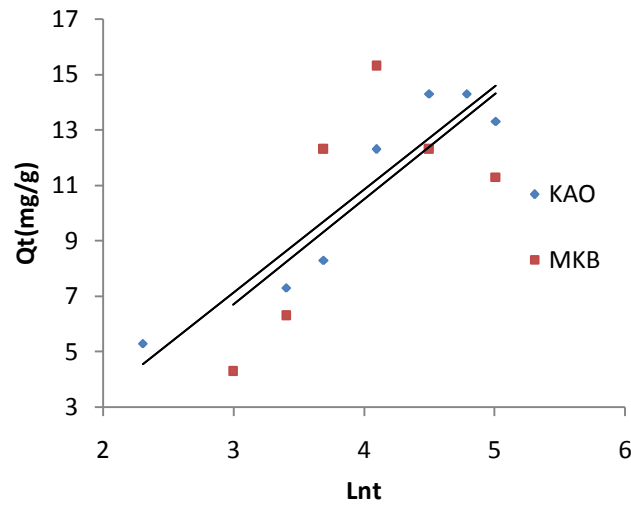

Figure 9. Elovich model's plot on Cu^{2+} ions adsorption on KAO and MKB
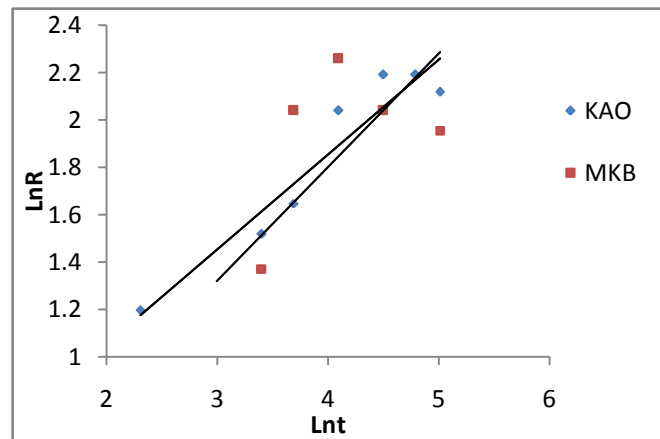

Figure 10. Intraparticle diffusion model's plot on Cu^{2+} ions adsorption on KAO and MKB

3.2.6 ADSORPTION ISOTHERMS STUDIES

Values of K and n are calculated from the intercepts and slopes of the plots of lnQe versus lnCe for Freundlich model. The term 1/n indicates the intensity of adsorption, in other words, the effectiveness of

adsorption. According to the Table 2, the adsorption is favorable, hence $1/n$ is less than unity. The determination coefficients, R^2, were used to compare the three isotherm models given by the figures 11, 12 and 13 below. As can be seen in Table 2, the Freundlich model showed a higher determination coefficient than the D-K-R and Temkin models.
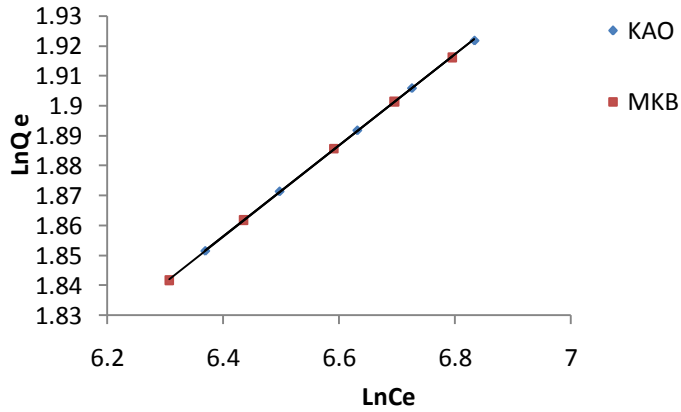

Figure 11. Freundlich model's plot for adsorption of Cu^{2+} ions on KAO and MKB
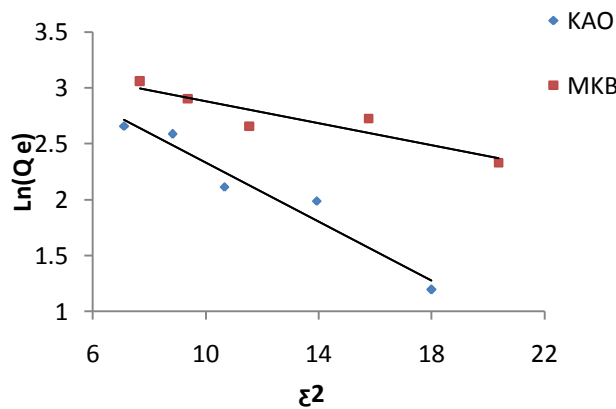

Figure 12. Dubinin-Kaganer-Raduskevich model's plot of Cu^{2+} ions on KAO and MKB.
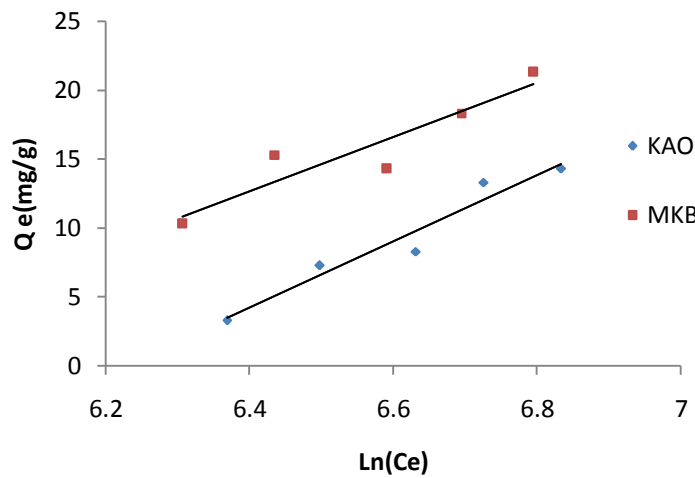

Figure 13. Temkin model's plot for adsorption of Cu^{2+} ions on KAO and MKB

Table 2: Kinetic models parameters of adsorption of Cu^{2+} ions onto KAO and MKB

Models	Parameters	Adsorbents	
		KAO	**MKB**
Pseudo-first order	**Q_{exp} (mg/g)**	14.300	12.300
	Q_e (mg/g)	11.020	10.270
	K_1 (min^{-1})	0.016	0.015
	R^2	0.998	0.996
Pseudo-second order	Q_e(mg/g)	16.940	14.080
	$K_2.10^{-3}$(g/mg.min)	2.040	3.190
	R^2	0.956	0.850
Elovich	β (g/min)	0.270	0.260
	α (mg/g.min)	1.268	1.120
	R^2	0.877	0.450
Intraparticle diffusion	K_{id} (min^{-1})	1.287	0.887
	α	-0.400	-0.479
	R^2	0.915	0.529
	K_o	0.006	0.005
	R^2	0.732	0.279

IV. CONCLUSION

The thermal modification of KAO was confirmed by FTIR spectroscopy, XRD and BET surface analysis techniques. The best conditions of adsorption were established, with respect to both pH and contact time to saturate the available sites located on the adsorbents surface. The pseudo-first-order kinetic and Freundlich isotherm models precisely explained the kinetic and equilibrium data respectively. The adsorption quantities were 14.3 mg/g and 12.3 mg/g for KAO and MKB respectivelyIn this study. Owing to the following results obtained, KAO and MKB can be used as adsorbents for the removal of Cu^{2+} ions from aqueous solution

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V. ACKNOWLEDGMENT

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