

Removal of Pb(II) ions from Aqueous Solutions by Kaolinite and Metakaolinite materials

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ABSTRACT

The study of the sorption of Pb(II) ions from aqueous solutions by low cost adsorbent materials like kaolinite (KAO) and synthetic metakaolinite (MET) was carried out experimentally using a batch sorption system at 27°C. The effects of pH, equilibrium contact time, adsorbent dose and adsorbate concentration were investigated. Sorption mechanism of Pb(II) ions on the surface of these two adsorbents were characterized through pseudo-first order, pseudo-second order, Elovich and intra-particle diffusion kinetic models. The results obtained show that contact time of 30 minutes was sufficient to attain equilibrium, both for KAO and MET. The maximum pH for Pb(II) adsorption was at 5.5. The maximum quantities adsorbed by each adsorbent were 2.37 mg/g for kaolinite and 1.34 mg/g for metakaolinite respectively. The most convenient model is the pseudo-second order, as per the linear regression coefficient values. Equilibrium data were analyzed by Langmuir, Freundlich and Temkin adsorption models. It was found out that the Langmuir and Temkin models were most suited in the description of the sorption of Pb(II) ions in aqueous solutions with very high R² values. These results show that KAO and MET display lower efficiency for the removal of Pb(II) ions from aqueous domestic and industrial effluents than commercial activated charcoal.

Keywords: Adsorption, Kaolinite, Metakaolinite, Kinetic models, Isotherm models

1. INTRODUCTION

Atmospheric, soil and water pollution by heavy metals is one of the most serious environmental and public health problems encountered nowadays [1]. Mostly from natural, industrial or anthropogenic origin, Lead (Pb) constitutes the most toxic of the heavy metals as it is not biodegradable and can accumulate in small but lethal doses in the human body and therefore causing its malfunctions [2,3]. Its presence in the surroundings constitutes a big danger to animal and plant life. Lead is ubiquitous and is a bluish-green trace metallic element [4]. Its extensive use worldwide many centuries ago is attributable to its extraction facility, malleability and low melting point. It has been used amongst other things as water pipes, glasswares, diverse objects (bullets), paints, textiles, ceramics, roofing, fuel additives, batteries, electronic

components and divers alloys for stabilizers [5]. After ingestion, Lead particles join the blood stream and are later distributed to the different organs like liver, kidney, spleen, brain, bones and central nervous system [6]. According to World Health Organisation, maximum tolerable concentrations of lead contained in water destined for human consumption is limited to less than 0.01 ppm [7, 8].

The treatment of aqueous wastes containing soluble heavy metal ions requires the concentration of metal ions followed by recovery for secure disposal. In compliance with the stipulated norms, many depollution techniques such as flocculation, chemical precipitation, solvent extraction, membrane processes (ion exchange or electrodialysis, reverse osmosis etc) and adsorption are used for wastewater treatment especially in the removal of metal ions [1]. The adsorption technique is most convivial and economically viable as the adsorbent is easily regenerated [9, 10]. The adsorptive properties of clay (cheap and non-toxic) for the removal of the pollutants are well documented. Most currently used adsorbents for heavy metal removal include organic materials such as marine algae [11], activated carbon prepared from green algae and *elais guineensis* [12]; malachite green [13] or inorganic such as goethite [14, 15], layered double hydroxides [16], laterite [17], calcites [18], used tyres and sawdust [19], activated carbon [20, 21], smectite [10, 22], zeolite [23, 24], hydrated Iron hydroxyde, and clay minerals such as kaolinites [25, 26]. In a previous study [18] in 2012, the maximum adsorption capacities of 200 mg/g and 150 mg/g Pb(II) of synthetic and natural calcite respectively, were obtained at initial lead loading of 1200 mg/L at 25 ± 2 °C. Other researchers have studied the adsorption of lead on oxide of silicon, manganese, aluminum, bentonite, dithizone-anchored poly (EDGMA-HEMA) microbeads [3]. Materials rich in silica and aluminium have shown greater efficiency in the removal of Lead from effluent sources. In this perspective, this work aims at investigating the adsorptive capacity of Kaolinites (natural and synthetic) with their rich chemical compositions in silica and aluminium, thus offering opportunities for its valorization in the reduction of Lead concentrations in the environment and contributing also to the adsorptive mechanism of Pb(II) ions onto natural kaolinites (KAO) and synthetic metakaolinites (MET).

2. MATERIALS AND METHODS

Raw samples of Kaolonite (KAO) which are made up of clay materials were collected locally from the south region of Cameroon. Metakaolinite (MET) were obtained from kaolinite by thermal activation (calcinations). Analysis of the chemical composition of KAO and MET show the following results for KAO: SiO₂(49.52); Al₂O₃(32.04); Na₂O (0.00); TiO₂(0.9864); Fe₂O₃(0.7526); K₂O(0.689); MgO(0.125); CaO(0.0406); SO₃(0.037); P₂O₅(0.034); NiO(0.0126); Cr₂O₃(0.011); CuO(0.0078); ZnO(0.0057); Ga₂O₃(0.005); Rb₂O(0.0047) and weight loss (15,73) for a total of 100.0014.

And for MET: SiO₂(46.99); Al₂O₃(34.66); Na₂O(10.55); TiO₂(0.941); Fe₂O₃(0.7889); K₂O(0.685); MgO(0.156); CaO(0.0606); SO₃(0.04); P₂O₅(0.03); NiO(0.0121); Cr₂O₃(0.01); CuO(0.0077); ZnO(0.006); Ga₂O₃(0.004); Rb₂O(0.0045) and weight loss (5.05) for a total of 99,9958.

2.1 Preparation of adsorbent

In order to enrich the collected clay samples in kaolinite before use, samples were soaked inside

distilled water for 24 hours, then washed in a 100 micron sieve immediately afterwards and finally were sun-dried. This procedure was repeated once but using a sieve of 80 microns. The kaolinitic product obtained ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) were oven dried à 110 °C for 25 hours. After drying, 500 g samples of the kaolinite were measured and grounded in a mortar to fine powder and sieved to 80 micron size. Metakaolinite was obtained from kaolinite by dehydroxylation in a muffle furnace maintained at 700 °C for 24 hours according to equation 1 below.



The carbonized material was taken out, grounded to fine powder and sieved to 80 micron size and stored in a vacuum dessicator.

2.2 Preparation of solutions

2.2.1 Stock solution of Pb(II) ions from solid lead nitrate (Chemical formula: $\text{Pb}(\text{NO}_3)_{2(s)}$), 97.5%, Riedel-de-Häen) was prepared by dissolving 1.5985g of the salt in 1 Liter of distilled water to give a concentration of 1000 ppm. The serial dilutions were made by diluting the stock solution in accurate proportions.

2.2.2 Ammoniacal buffer solution was prepared by dissolving 67.5 g of NH_4Cl (97%, Riedel-de-Häen) inside 570 mL of concentrated NH_3 (25%, Riedel-de-Häen) and making up to 1Liter with distilled water.

2.2.3 100 ppm solution of dithizone was prepared by dissolving 0.005g of dithizone ($\text{C}_6\text{H}_5\text{NHNHCSNNC}_6\text{H}_5(s)$, 98%; Fluka) inside ethanol ($\text{CH}_3\text{CH}_2\text{OH}(l)$, 98%, Riedel-de-Häen) contained inside 250- mL volumetric flask.

2.2.4 pH adjustment solutions were prepared using nitric acid (0.1M, 60%, Riedel-de-Haen) and sodium hydroxide (0.1M from 98%, Fluka) solutions respectively.

2.2.5 Complexe solution was prepared by adding 2 mL of dithizone and 2 mL of the ammoniacal buffer solution into the filtered solutions of the Pb(II) ions for its determination by spectroscopy.

2.3 Batch adsorption experiments

Equilibrium and kinetic adsorption experiments were carried out in a temperature controlled batch adsorption reactor maintained at 27 °C. All the experiments (except the study of the effect of pH) were carried out at pH of 6.5. For each experiment (except otherwise stated), 0.5 g of adsorbent were measured and put into a 250-mL conical flask containing 20 mL of the Pb(II) ions at the desired concentration that ranged between 10 through 120 ppm in this study. After agitating the solution for a given or predetermined time interval (20-120 minutes) with a magnetic agitator, samples were then filtered, thus separating the solid/adsorbent from the liquid/solution phase. The filtered solution was put into a test tube containing dithizone and ammoniacal buffer solutions respectively to form a complexe. The concentration of the residual Pb(II) ions were determined *spectrometrically* using a UV-visible spectrophotometer CORNING6259 at $\lambda_{\text{max}} = 490 \text{ nm}$. Adsorption data obtained from equilibrium studies (contact time and initiation concentration effects) were employed in the kinetic studies and the applicability of different adsorption isotherms

to Pb(II) ions. The percentage removal efficiency of the adsorbents (%R), which is the sorption capacity at time t and the sorption capacity at equilibrium are calculated as follows:

$$\begin{aligned}\% (R) \text{ adsorption} &= 100(C_o - C_t)/C_o \\ Q_t(\text{mg/g}) &= (C_o - C_t)V/m \\ Q_e(\text{mg/g}) &= (C_o - C_e)V/m\end{aligned}\quad (2)$$

Where $C_o(\text{mg/L})$ and $C_t(\text{mg/L})$ are the liquid-phase concentrations of solute (adsorbate) at the origin and at a given time t, respectively. $C_e(\text{mg/L})$ is the equilibrium concentration of Pb(II) ions, $V(\text{L})$ is the volume of the solution while $m(\text{g})$ is the mass (m) of the adsorbent.

3.4 Kinetic Models

Adsorption kinetics describes the relationship between the rate of solute uptake and adsorption time. In order to verify the adsorption kinetic models, the pseudo-first-order, the pseudo-second-order, the Elovich and intraparticle diffusion models are applied to the experimental raw data.

3.4.1 Pseudo-first-order model

This model is based on the assumption that the adsorption rate is proportional to the number of available sites [27] and is calculated by the following equation:

$$dQ_t/dt = K_f(Q_e - Q_t) \quad (3)$$

Where Q_t and $Q_e(\text{mg/g})$ are the amounts of adsorbate retained per unit weight of adsorbent at given time and at equilibrium respectively. $K_f(\text{min}^{-1})$ is the rate constant of the adsorption process.

By integrating between $t = 0$ and $t = t$ corresponding to $Q_t=0$ and $Q_t = Q_t$, we obtain the following:

$$\ln(Q_e - Q_t) = \ln Q_e - K_f t \quad (4)$$

Linear plots of $\ln(Q_e - Q_t)$ versus t can be carried out in order to interpret or evaluate this kinetic model and to determine Q_e and the rate constant from the intercept and slope respectively.

3.4.2 Pseudo-second-order model

It is based on the assumption that adsorption rate is proportional to the square of the number of unoccupied sites [28]:

$$dQ_t/dt = K_s(Q_e - Q_t)^2 \quad (5)$$

where $K_s(\text{mg.g}^{-1}.\text{min}^{-1})$. By integrating between $t=0$ and $t=t$ corresponding to $Q_t=0$ and $Q_t = Q_t$, we obtain the following:

$$t/Q_t = 1/K_s Q_e^2 + t/Q_e \quad (6)$$

The parameters K_s and Q_e can be calculated from the intercepts and the slope of the graph of t/Q_t versus t.

3.4.3 Elovich model

Elovich equation is a rate equation based on the adsorption capacity $Q_t(\text{mg/g})$, an equation that can be expressed as [9]:

$$dQ_t/dt = \alpha e^{-\beta Q_t} \quad (7)$$

where α = initial adsorption rate ($\text{mg.g}^{-1}.\text{min}^{-1}$) and β is related to the extent of surface coverage and activation energy for chemisorptions (g/mg)

By integrating between $t=0$ and $t=t$ corresponding to $Q_t=0$ and $Q_t=Q_t$, we obtain the following after some simplifications:

$$Q_t = \ln(\alpha\beta)/\beta + \ln t/\beta \quad (8)$$

The value of the constants can be obtained from the slope and intercepts of a plot of Q_t versus $\log t$.

3.4.4 Intra-particle diffusion model

The intra-particle diffusion model equation can be written as follows [29]:

$$Q_t = K_{id} t^{1/2} + C, \quad (9)$$

where K_{id} is the inter-particle rate constant ($\text{mg.g}^{-1}.\text{min}^{-1/2}$) and C is the intercept. By plotting $Q_t(\text{mg.g}^{-1})$ versus $t^{1/2}$ one should obtain a linear graph if the intra-particle diffusion is involved in the adsorption process. If the straight line passes through the origin, the intra-particle diffusion is the rate limiting step [29].

3.5 Adsorption models

There are a number of sorption models developed to describe the adsorption mechanism and to fit the experimental adsorption data. In the present study on the investigation of the mechanism of the adsorption of Pb(II) ions on some Cameroonian clays, we have used three models: the Langmuir isotherm, the Freundlich isotherm and the Temkin equation respectively.

3.5.1 The Langmuir isotherm.

The mathematical expression of the Langmuir isotherm can be written as [10]:

$$Q/Q_m = KC_e/(1+KC_e) \quad (10)$$

In this equation C_e is the bulk equilibrium concentration of adsorbate in solution, K is an affinity constant, Q is the amount of the adsorbate that is adsorbed at equilibrium concentration C_e and

Q_m is the amount that is necessary to cover the surface by a monolayer of adsorbate. In this adsorption isotherm, an assumption is made that the energy of adsorption is constant at all concentrations up to the full coverage of the surface. The Langmuir equation can be rewritten in linear form as:

$$C_e/Q = 1/K.Q_m + C_e/Q_m \quad (11)$$

Equation (11) implies that a graph of C_e/Q versus C_e should result in a straight line.

3.5.2 Freundlich Isotherm

Another type of equation which has been used in this work to fit the adsorption data is the Freundlich equation, which can be written as [10]:

$$Q = K_d C_e^{1/n} \quad (12)$$

In this equation, Q is the amount adsorbed at the surface; C_e is the equilibrium concentration of

adsorbate in solution, K_d is the distribution coefficient and n is a correction factor related to the heterogeneity of the surface. Taking the logarithm of either sides of this equation, it can be rewritten as:

$$\ln Q = 1/n \ln C_e + \ln K_d \quad (13)$$

From which we see that a plot of $\ln Q$ versus $\ln C_e$ should give rise to a straight line with the slope of $1/n$ and intercept equal to $\ln K_d$ if the adsorption follows a Freundlich isotherm. Still another type of equation which has been applied to our adsorption data is the:

3.5.3 Temkin isotherm.

It is expressed in linear form by the following relationship between the amount adsorbed and concentration in solution [30]:

$$Q_e = B(\ln K_T + \ln C_e) \quad (14)$$

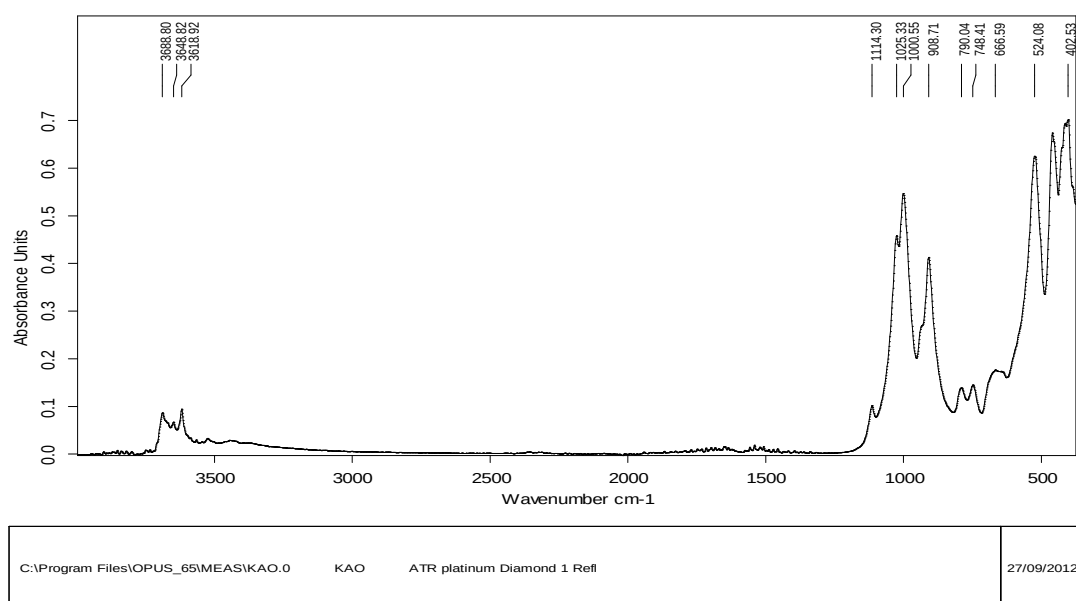
where $B = RT/b$ is related to the heat of adsorption, T is the absolute temperature, R is the universal gas constant. B indicates the adsorption potential of the adsorbent and K_T is the equilibrium binding constant. Similar to the Freundlich equation, the Temkin model takes into account the heterogeneity of the surface [31].

3. Results and Discussion

3.1 Characterization of adsorbent

FTIR spectroscopy was used to characterize the Kaolinite (KAO) and synthetic metakaolinite (MET) samples as illustrated in Figures 1 and 2 below.

The analysis of the first spectrum (figure 1) show absorption bands at 3693 cm^{-1} ; 3656 cm^{-1} ; and 3620 cm^{-1} which corresponds to stretching vibrations of the hydroxyl (OH) of KAO, and average band at 1110 cm^{-1} by the Si-O functional group and at $1000, 1025, 402 \text{ cm}^{-1}$ for symmetric and asymmetric vibration of the Si-O-Si group. We also perceived a small band at 908 cm^{-1} for the deformation of the Al-OH bond of the KAO. Also present is another band between $790\text{-}748 \text{ cm}^{-1}$ which are translational vibration bands for Si-O-Al and finally a Si-O-Si characteristic band of KAO at 666 cm^{-1} is visible.



Seite 1 von 1

Figure 1: IR spectra of Kaolinite on platinum in KBr matrix.

We observe on the second spectrum (figure 2 below) that all the vibrational bands due to the hydroxyl group (OH) are absent and only characteristic absorption bands for the Si-O at 1042 cm^{-1} , for Si-O-Al at 787 cm^{-1} and 542 cm^{-1} respectively are present.

3.2 Effect of contact time

Figure 3 shows the effect of contact time on the adsorbate uptake. The experiment was carried out at pH 6.5 by agitating 60 mL of the aqueous Pb(II) ions ($C_0 = 60\text{ mg/L}$) with 0.5 g of adsorbent (KAO and MET) at $27\text{ }^{\circ}\text{C}$. The contact time ranged between 20-120 minutes. The uptake of Pb(II) ions onto the adsorbents nearly reached equilibrium after 30 minutes and based on these results, it was later considered as equilibrium time throughout our study. It is inferred from this figure that for the same contact time and adsorbent dose, KAO shows more adsorption potentials (2.37 mg/g) than MET (1.34 g/g) under these experimental conditions. We noticed here that adsorption takes place in two stages. The first phase happens between 0-20 minutes and is attributed to the presence of free adsorption sites at the adsorbent surface. Once Pb(II) ions are successfully adsorbed, the progressive occupation of these sites comes to a halt giving rise to a plateau which puts into evidence the equilibrium time of contact which in this case is 30 minutes for KAO and MET respectively.

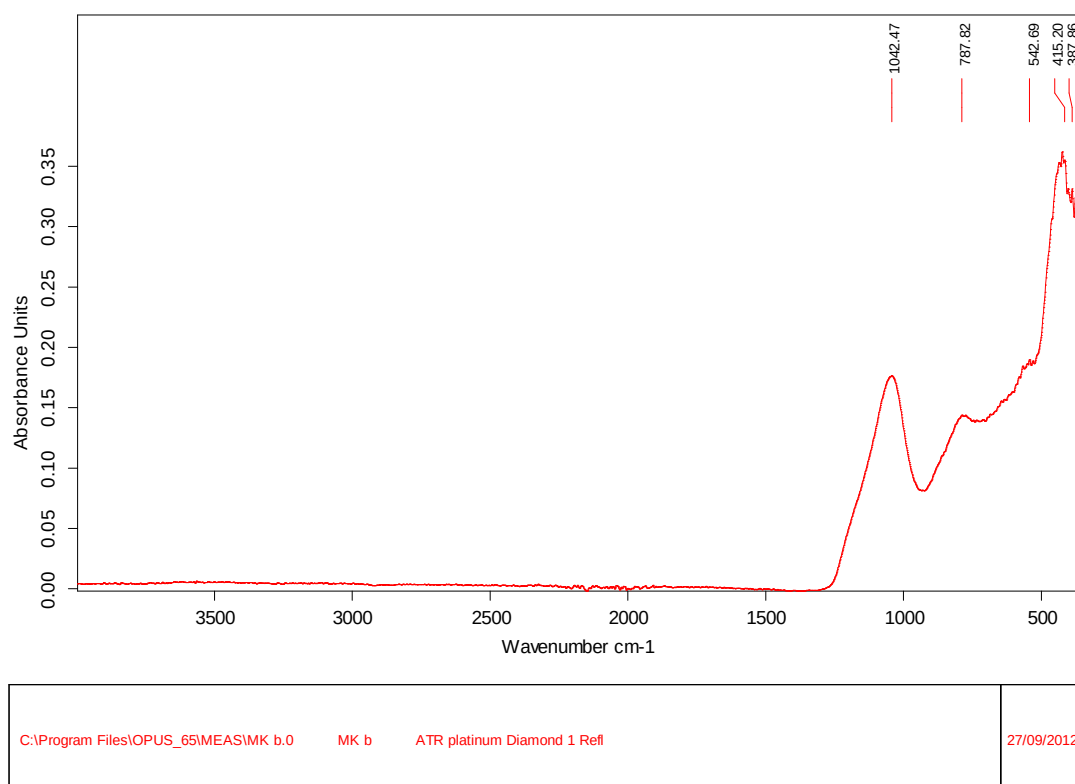


Figure 2: IR spectrum of metakaolinite on platinum film inside KBr matrix.

3.3 Effect of Adsorbent Dosage

The influence of the adsorbent concentration on the removal of Pb(II) ions from aqueous solution was studied by varying the mass (m) of each adsorbent. For each trial, a sample of the adsorbent with a given mass was mixed with 20 mL of an aqueous solution of Pb(II) ions (80 mg/L) and the resultant mixture allowed to equilibrate for 30 minutes at pH 6.5. Also inferred by this result (Figure 4) is the fact that more than 80% removal of Pb(II) ions for both KAO and MET were obtained just for adsorbent weight ranging between 0.1-0.2 g. The adsorption capacity of the adsorbents (that is Pb(II) ion removal) are higher at the beginning probably because of more available area as a result of smaller concentration of the adsorbent for the adsorption process. The percentage removal, however, decreased with increasing adsorbent dose. This is explained by the fact that an increase in adsorbent dose leads to an agglomeration of unit cells and consequently a decrease in intercellular distances which in turn produces a screening effect leading to the protection of the adsorption sites of the adsorbent.

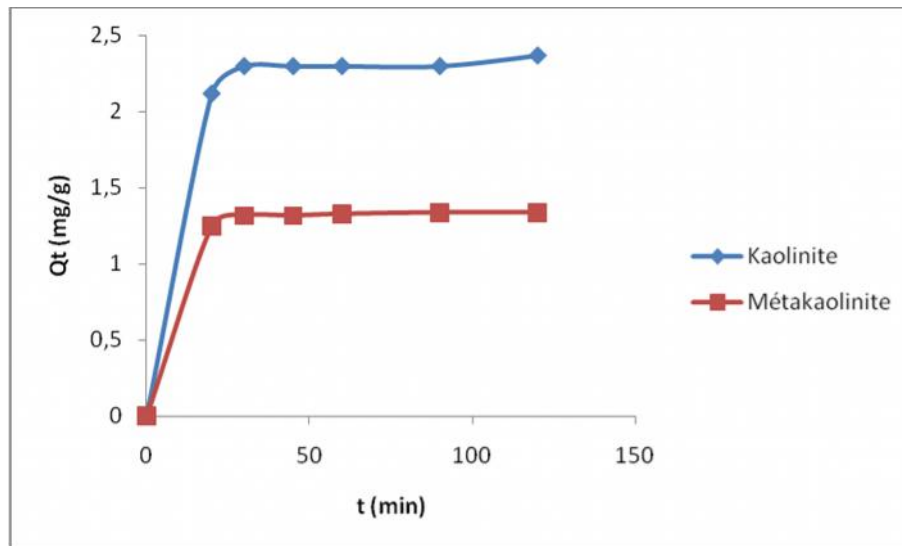


Figure 3: Effect of contact time on the adsorption of Pb(II) ions. (Conditions: 20mL, 60mg/L Pb(II) solution ; 0.5g KAO , 0.5g MET)

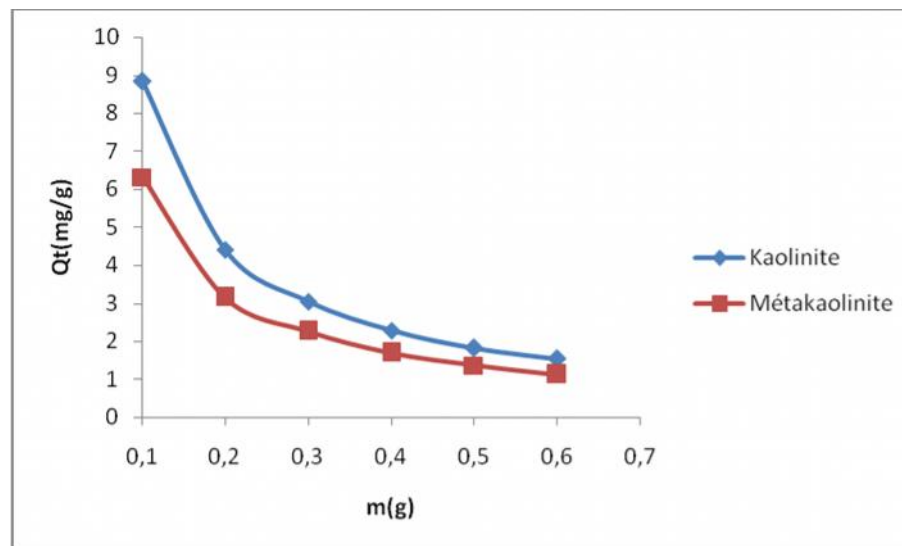


Figure 4: Effect of adsorbent dosage on the adsorption of Pb(II) ions (conditions : 20mL, 80mg/L Pb(II) solution, pH= 6.5, t_e = 30min)

3.4 Effect of Initial Concentration

On the basis of the results of the preceding paragraph, the analysis of the effect of the initial concentration of Pb(II) ions were henceforth carried out at pH 5.5 on adsorbent samples (both KAO and MET) of 0.1 g each, mixed with 20 mL of the aqueous solution at 27 °C for a duration of 30 minutes.

The outcome of this set of experiments (Figure 5) show that the quantity of Pb(II) ions adsorbed changes

from 5.85 mg/g to 9.30 mg/g for KAO, 5.09 mg/g to 8.56 mg/g for MET, for a concentration range between 40 and 120 ppm. This is attributable to the availability of active sites at higher initial concentration of Pb(II) in the aqueous solutions. The adsorption sites take up the available adsorbate ions more quickly at higher concentrations as a result of increase collision probability with concentration increases. This result also show that maximum adsorption capacity for both adsorbents KAO and MET is reached at initial adsorbate concentrations of 120 ppm. We can also gather from these results that KAO exhibits higher adsorption capacity than MET. This observation is attributable to the fact that KAO has many more hydroxyl groups on its surface than MET, which signifies greater electrostatic attractions for the Pb(II) ions in solution.

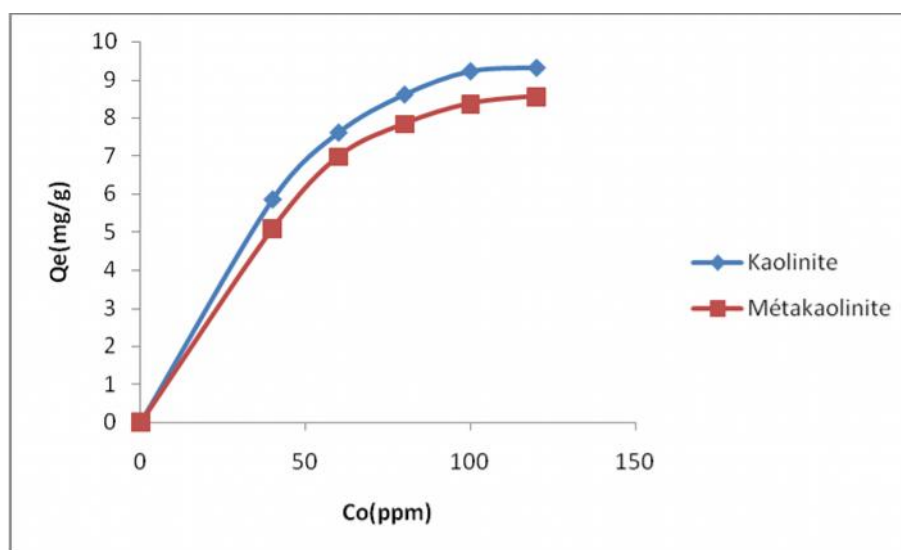


Figure 5: Influence of Pb(II) ion initial concentration on its adsorption on KAO and MET. (conditions: 0.1g KAO et 0.1g MET, 20mL Pb(II) solution, 30min pour KAO and MET, pH 5.5)

3.5 Effect of pH

Figure 6 shows the effect of pH on the adsorption of Pb(II) ions onto KAO and MET. The effect of pH was investigated between pH range of 2.5 -7.5, initial pH controlled by the addition of 0.1M HNO₃ or 0.1 M NaOH solutions agitated with 0.1 g of adsorbent for 30 minutes at an initial 60 mg/g concentration of Pb(II) ion solutions. As can be seen in this figure, there is slight increase in adsorption of Pb(II) ions as solution pH passes from 2.5 towards 7. In the case of KAO, the quantity adsorbed falls slightly at very acidic pH before reaching its equilibrium at pH 5.5. This result is due to the formation of soluble hydroxyl complexes at the surface of KAO, which when dissociated leads to no further changes in pH. In the case of MET, the pH is more or less constant at the start and then increases slightly to its maximum value at pH 5.5, probably due to the precipitation of some Pb(II) ions [32]. So, for further experiments pH was maintained at 5.5 throughout.

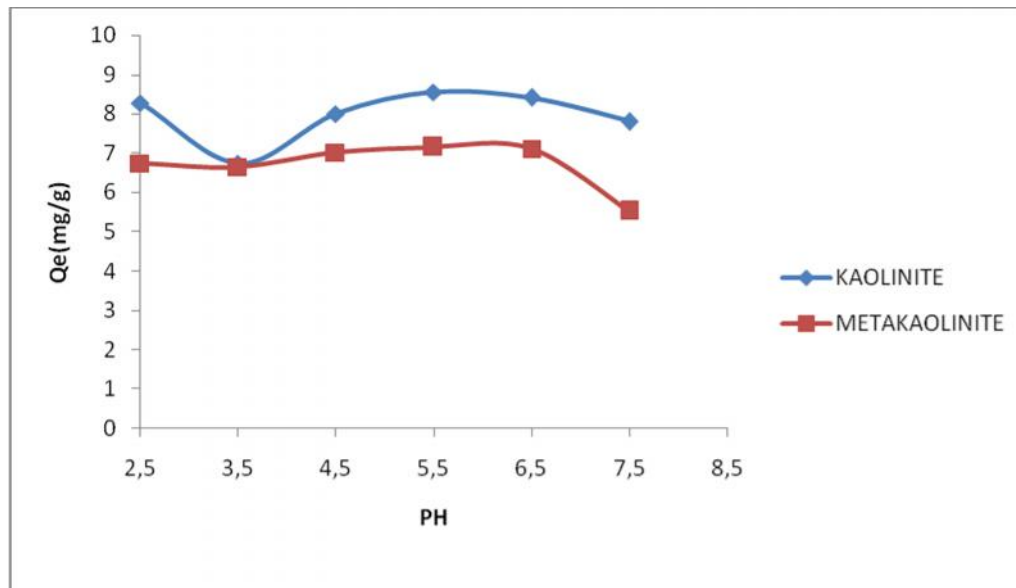


Figure 6: Effect of pH of Pb(II) solution on adsorption (conditions : 20mL, 60mg/L Pb (II) solution ; 0.1g KAO, 0.1g MET, $t_e=30$ min, for KAO and MET)

3.4 Adsorption kinetics

Adsorption kinetics of Pb(II) ions were studied following four kinetic models. In order to obtain the parameters relative to each kinetic model, experimental results were tested for linear best fits. Figures 7 and 8 show some linear relationships between adsorbed quantities and time while the characteristic parameters are given on table 1 for each kinetic model. These results show that the adsorption of Pb(II) ions on KAO and MET are best described by pseudo-second order kinetic models with high correlation coefficient of the order 0.999, therefore suggesting that the rate is limited by chemisorptions. Different kinetic behaviors (rate constants) for each adsorbent are a result of the structural differences that exist between them (Rajesh *et al.*, 2010). Low correlation coefficients and gradients obtained with the inter-particle diffusion model means that that this model is not obeyed by KAO and MET adsorbents. This result means that Pb(II) ions slowly diffuse into the pores of the different adsorbents and therefore constitute a limiting step [33].

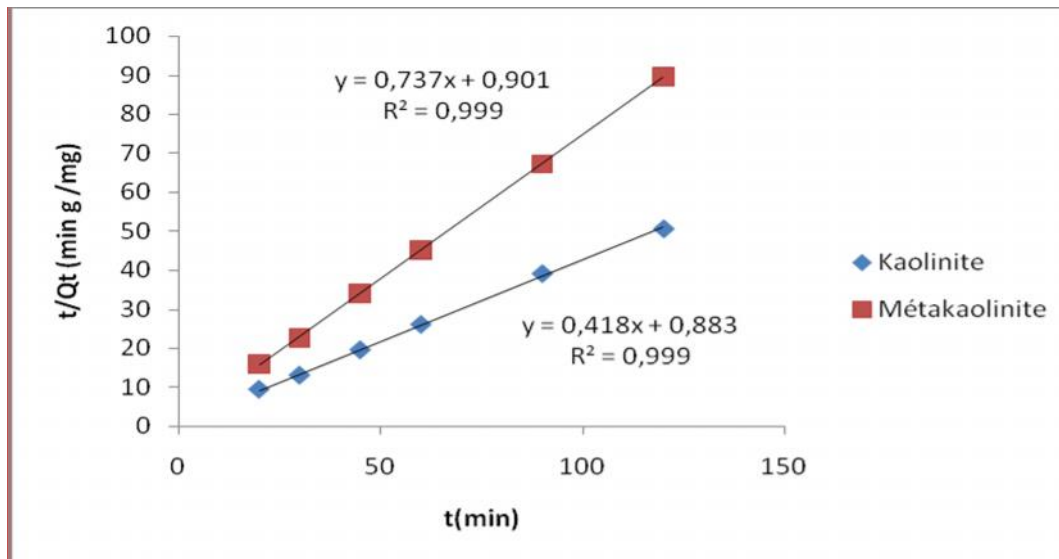


Figure 7 : Linear transformation of second order kinetic model at 60mg/L and pH 5.5

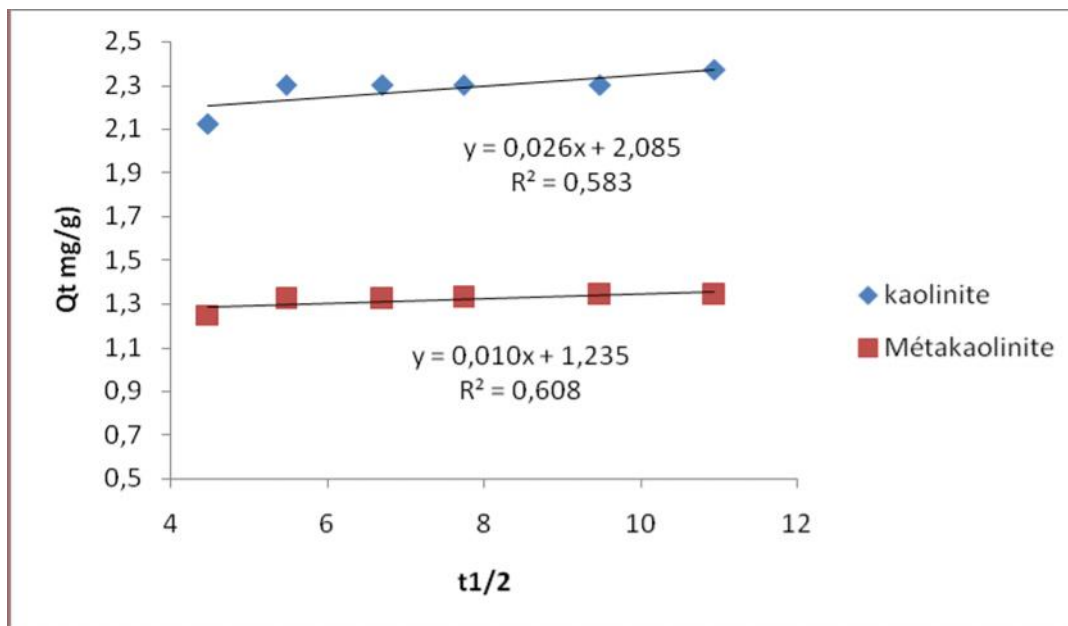


Figure 8: Linear transformation of intra-particle diffusion model at 60mg/L at pH 5.5

Table 1: Results of kinetic plots for the adsorption of Pb(II) onto KAO and MET

Adsorbent			KAO	MET
C_0 (mg/L)			60 ppm	
Pseudo-first-order	K_1 (min ⁻¹)		0.000	0.000
	Q_e (mg/g)		105.53	62.05
	R^2		0.471	0.588
Pseudo-second-order	K_2 (g/min.mg)		0.54	0.17
	Q_e (mg/g)		1.35	2.39
	R^2		0.999	0.999
Elovich kinetic model	α (mg/g min)		2.95×10^7	3.19×10^{10}
	β (g/mg)		10.30	23.809
	R^2		0.639	0.709
Intra-particle diffusion model	K_d (mg/g min ^{1/2})		0.026	0.010
	C (mg/g)		2.085	1.235
	R^2		0.583	0.608

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322 3.5 Adsorption Isotherms

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Equilibrium studies of the adsorption of Pb(II) ions in aqueous solutions by KAO and MET have been carried out according to three models as indicated above. Table 2 presents a summary of the Langmuir constants, Q_m and K_L obtained by plotting C_e/q_e as a function of C_e (figure 9). The maximum adsorption capacity (monolayer) for KAO and MET are 10.416 mg/g and 10.104 mg/g respectively. Also from the results of this undertaking we inferred that $K_L < 1$ for the range of concentration studied, hence, the sorption of Pb(II) ions on the two adsorbents are favorable according to Langmuir isotherm. On the other hand, and in consideration of the Freundlich isotherms (figure 10), since $0 < 1/n < 1$ in both cases of adsorbents, we conclude that adsorption is also favorable. On table 2 is also depicted the results of Temkin isotherm (figure 11) obtained by displaying q_e versus $\ln C_e$ from which we deduce that the adsorption energy variation B_T is positive (endothermic reaction) both for KAO and MET [34]. Given that the values of B_T are all less than 8kJ/mol, the interaction between adsorbents and adsorbate (Pb(II) ions) are weak and therefore the adsorption mechanism put into play here is merely that of ion exchange.

From these equilibrium studies, the adsorption of Pb(II) ions in aqueous solution onto KAO and MET is satisfactorily described by the Langmuir isotherm model ($R^2 \geq 0.999$) ; a less satisfactory description by the Temkin model is a clear indication of a monolayer adsorption process, and translated by a decrease in attraction adsorbent surface and Pb(II) ions with increase in separation distance [35].

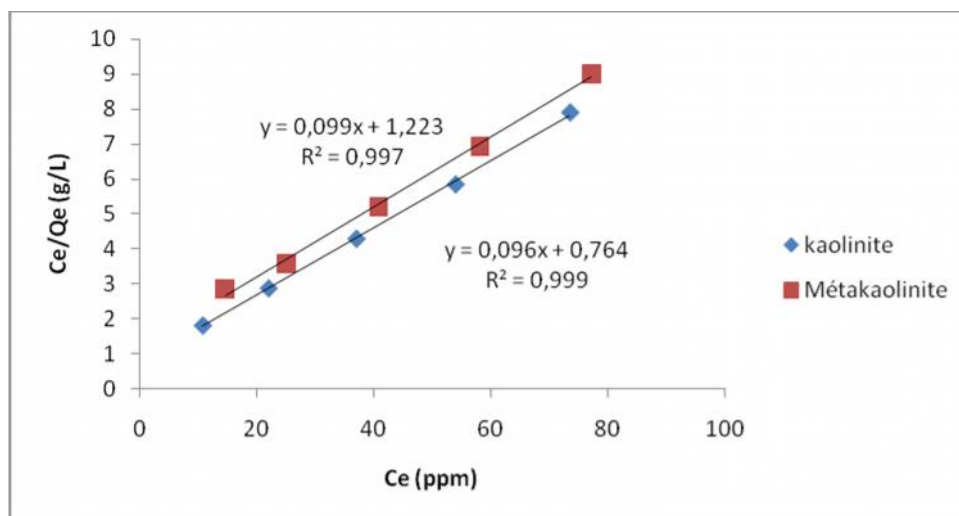


Figure 9: Linear transformation of Langmuir isotherm

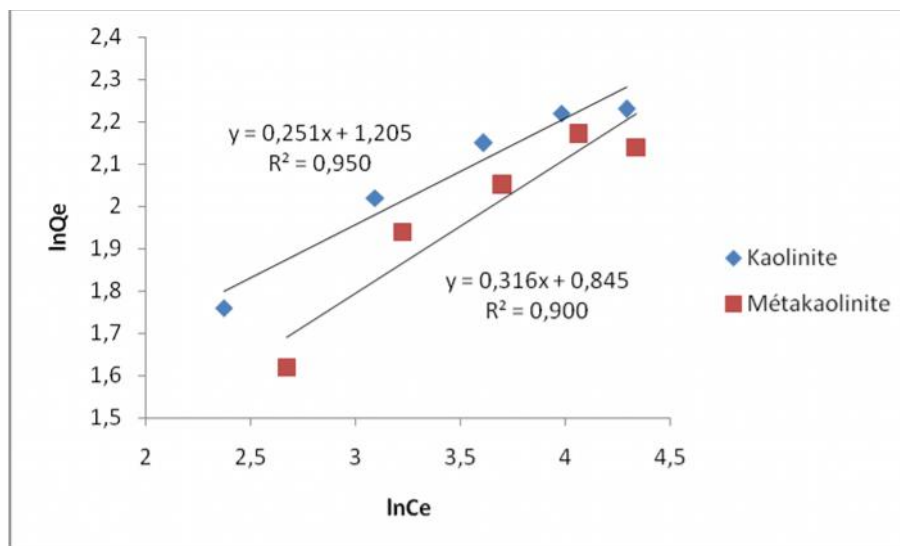


Figure 10: Linear transformation of Freundlich isotherm

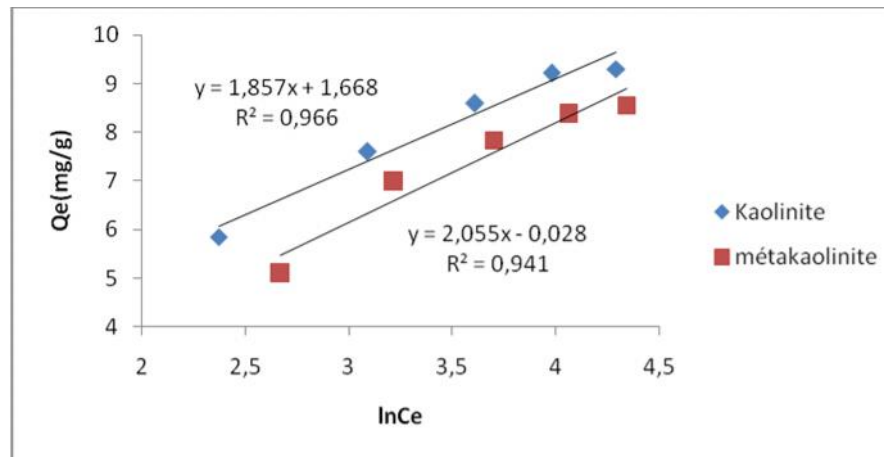


Figure 11: Linear transformation of the Temkin isotherm

Table 2: Summary of isotherm plots for the adsorption of Pb(II) onto KAO and MET

Modèle	Langmuir			Freundlich			Temkin		
Paramètre	K_L (L/mg)	Q_m (mg/g)	R^2	K_F (L/mg)	$1/n$	R^2	A_T (L/g)	B_T (J/mol)	R^2
KAO	0.125	10.416	0.999	3.336	0.251	0.950	2.455	1343.805	0.966
MET	0.080	10.101	0.997	2.327	0.316	0.900	0.986	1214.329	0.941

Separation factors for the different concentrations have been depicted on table 3 below. All the values are less than unity in the range of concentrations envisaged in this study, implying that Langmuir adsorption isotherm best describes the adsorption of Pb(II) ions in aqueous solution onto KAO and MET.

Table 3: Separation factor, R_L for concentrations

Concentration (ppm)	40	60	80	100	120
KAO	0.166	0.117	0.090	0.074	0.062
MET	0.238	0.172	0.135	0.111	0.094

4. CONCLUSION

The principal objective of this research undertaking has been to valorize some southern Cameroonian clay in their decontamination capacity of municipal effluents containing a toxic heavy metal ions like Pb(II). Results of our study on KAO and MET show that both adsorbents manifest some effectiveness in the elimination of the Pb(II) ions in solutions. The most convenient adsorption kinetic model for both adsorbents was the pseudo-second-order. Langmuir adsorption isotherm best described the adsorption of Pb(II) ions in aqueous solutions onto KAO and MET respectively. Therefore, on the basis of our experimental results and the model parameters obtained thereof, it can be inferred that the adsorbents

from natural origin like clay minerals (KAO and MET) are not very effective in the removal of Pb(II) ions from aqueous solutions as compared to commercial activated carbon adsorbents.

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7. Figure Captions

Figure 1: IR spectra of Kaolinite on platinum in KBr matrix.

Figure 2: IR spectrum of metakaolinite on platinum film inside KBr matrix.

Figure 3: Effect of contact time on the adsorption of Pb(II) ions. (*Conditions: 20mL, 60mg/L Pb(II) solution ; 0.5g KAO , 0.5g MET*)

Figure 4: Effect of adsorbent dosage on the adsorption of Pb(II) ions (*conditions : 20mL, 80mg/L Pb(II) solution, pH= 6.5, t_e = 30min*)

Figure 5: Influence of Pb(II) ion initial concentration on its adsorption on KAO and MET. (*conditions: 0.1g KAO et 0.1g MET, 20mL Pb(II) solution, 30min pour KAO and MET, pH 5.5*)

Figure 6: Effect of pH of Pb(II) solution on adsorption (*conditions : 20mL, 60mg/L Pb (II) solution ; 0.1g KAO, 0.1g MET, t_e =30 min,for KAO and MET*)

Figure 7: Linear transformation of second order kinetic model at 60mg/L and pH 5.5

Figure 8: Linear transformation of intra-particle diffusion model at 60mg/L at pH 5.5

Figure 9: Linear transformation of Langmuir isotherm

Figure 10: Linear transformation of Freundlich isotherm

Figure 11: Linear transformation of the Temkin isotherm