Removal of Pb(II) Ions from Aqueous Solutions by Kaolinite and Metakaolinite Materials

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Authors' contributions

This work was carried out in collaboration between all authors. Authors JNG and MJK designed and supervised the study. Author JNG also wrote the first draft of the article. The second author managed the analyses of the study, carried out the literature searches while the fourth author wrote the protocol. All authors read and approved the final manuscript.

ABSTRACT

Aims: To study the sorption of Pb(II) ions from aqueous solutions by low cost adsorbent materials like kaolinite (KAO) and synthetic metakaolinite (MET) in order to validate the effects of *pH*, equilibrium contact time, adsorbent dose and adsorbate concentration. To investigate the sorption mechanism of Pb(II) ions on the surface of these two adsorbents through pseudo-first order, pseudo-second order, Elovich and intra-particle diffusion kinetic models.
Study Design: We used a batch sorption system at 27 ⁰C and operated at constant *pH* equal to 5.5.
Place and Duration of Study: Department of Chemistry, University of Dschang, Cameroon and Department of Inorganic Chemistry, University of Yaounde I, Cameroon, between July 2012 and September 2012.
Methodology: For each experiment (except otherwise stated), 0.5 g of adsorbent was 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 and 120 ppm and later on agitated, filtered and analyzed by UV-Visible spectroscopy.
Results: Equilibrium was attained after a contact time of 30 minutes both for KAO and

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MET. Maximum *pH* for Pb(II) adsorption was at 5.5 and was therefore maintained at that value throughout. 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 was the pseudo-second order, as per the linear regression coefficient values (r^2). Equilibrium data were analyzed by Langmuir, Freundlich and Temkin adsorption models. It was inferred that the Langmuir and Temkin models (with very high r^2 values) were most suited to describe the sorption of Pb(II) ions in aqueous solutions.
Conclusion: 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 carbon and others from diverse origins.

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 and thus become a risk factor for human health [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 in water pipes, glasswares, diverse objects (bullets), paints, textiles, ceramics, roofing, fuel additives, batteries, electronic components and divers alloys for stabilizers [5] amongst other things. After ingestion, lead particles enter the blood stream and are later distributed to the different organs like the liver, kidney, spleen, brain, bones and central nervous system [6]. According to the World Health Organisation, maximum tolerable concentrations of lead in water for human consumption is limited to less than 0.01 ppm [7,8]. Therefore, the elimination of Pb(II) from effluents is crucial for environmental pollution cleaning.

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 in particular in the removal of metal ions [1]. The adsorption technique is most convenient and economically viable as the adsorbent is easily regenerated [9,10]. 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 inorganics 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 [23,24,25], hydrated Iron hydroxide, and clay minerals such as kaolinites [26, 27],magnetic iron oxide [27], multiwall carbon nanotubes [28,29], diatomite [30]. Recently, the elimination of Pb(II) ions from effluent sources by various adsorbents have been a major preoccupation [25,28,29,30,31,32]. In the literature for example [18], maximum adsorption capacities of 200 mg/g and 150 mg/g Pb(II) of synthetic and natural calcite respectively, were obtained at an initial lead loading of 1200 mg/L at 25±2ºC. The adsorption of Pb(II) ions on magnetic composite of β-cyclodextrin grafted onto multiwall carbon nanotubes/iron oxides/CD was also found to be dependent on *pH* while the adsorption of 1-naphtol was *pH* independent

[28]. These authors attributed the enhancement of the adsorption capacity to the strong abilities of the multiple hydroxyl groups and the inner cores of the hydrophobic cavity in β-CD to form complexes with metal ions and organic pollutants. The sorption of Pb(II) ions on NKF-6 Zeolite was also reported to be dominated by ion-exchange or outer-sphere surface complexation at low *pH* values,and by inner-sphere surface complexation at higher *pH* values [25]. Other researchers have studied the adsorption of lead on oxides of silicon, manganese, aluminum, bentonite, and dithizone-anchored poly (EDGMA-HEMA) microbeads [3]. The adsorptive properties of clay (cheap and non-toxic) for the removal of the pollutants are well documented. These materials rich in silica and aluminium have shown a greater efficiency in the removal of lead from effluent sources [10]. In this perspective, this work aims at investigating the adsorptive capacity of Kaolinites (natural and synthetic) with their rich chemical compositions of in silica and aluminium, thus offering opportunities for its evaluation in the reduction of lead concentrations in the environment and understanding the -adsorptive mechanism of Pb(II) ions onto natural kaolinites (KAO) and synthetic metakaolinites (MET).

2. MATERIALS AND METHODS

Raw samples of Kaolinite (KAO) which are made up of clay materials were collected locally from the southern region of Cameroon. Metakaolinite (MET) was obtained from kaolinite by thermal activation (calcinations). Analysis of the chemical composition of KAO and MET showed the following results for KAO: SiO_2(49.52); Al_2O_3(32.04); Na_2O (0.00); TiO_2(0.9864); Fe_2O_3(0.7526); K_2O(0.689); MgO(0.125); CaO(0.0406); SO_3(0.037); P_2O_5(0.034); NiO(0.0126); Cr_2O_3(0.011); CuO(0.0078); ZnO(0.0057); Ga_2O_3(0.005); Rb_2O(0.0047) and weight loss (15,73) for a total of 100.0014.

Similarly for MET*:* SiO_2(46.99); Al_2O_3(34.66); Na_2O(10.55); TiO_2(0.941); Fe_2O_3(0.7889); K_2O(0.685); MgO(0.156); CaO(0.0606); SO_3(0.04); P_2O_5(0.03); NiO(0.0121); Cr_2O_3(0.01); CuO(0.0077); ZnO(0.006); Ga_2O_3(0.004); Rb_2O(0.0045) and weight loss (5.05) for a total of 99,9958.

2.1 Preparation of Adsorbent

In order to enrich the kaolinite concentration in the collected clay samples before use, the samples were soaked in distilled water for 24 hours, then washed in a 100 micron sieve. This procedure was repeated once but using a sieve of 80 microns. They were then separated from water by decantation and finally sun-dried. After drying, 500 g samples of the kaolinite were measured and ground in a mortar to fine powder and sieved through an 80 micron filter. The kaolinitic products obtained ($Al_2Si_2O_5(OH)_4$) were oven dried at 110ºC for 25 hours in order to remove any organic or remaining water molecules. After drying at this temperature, samples were kept in a dessicator for subsequent adsorption process. Metakaolinite was obtained from kaolinite by dehydroxylation in a muffle furnace maintained at 700 ºC for 24 hours according to equation 1 below.

$$Al_2O_3.2SiO_3.2H_2O \longrightarrow Al_2O_3.2SiO_3 + 2H_2O \qquad (1)$$
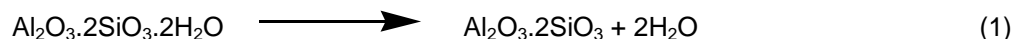
The carbonized material was taken out, ground to fine powder and passed through an 80 micron sieved, dried at 110ºC for 24 hours before being stored in a vacuum dessicator.

2.2 Preparation of Solutions

2.2.1 The stock solution of Pb(II) ions from solid lead nitrate (Chemical formula: $(Pb(NO_3)_{2(s)})$, 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. Standard solutions were prepared by diluting the stock solution in accurate proportions.

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

2.2.3 100 ppm solution of dithizone was prepared by dissolving 0.005g of dithizone $(C_6H_5NHNHCSNNC_6H_{5(s)}$, 98%; Fluka) inside ethanol $(CH_3CH_2OH_{(l)}$, 98%, Riedel-de-Häen) contained inside a 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.

2.2.5 The 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 investigation by spectrophotometric titration.

2.3 Batch Adsorption Experiments

Equilibrium and kinetic adsorption experiments were carried out in a temperature controlled batch adsorption reactor maintained at $27^{\circ}C$. All the experiments (except the study of the effect of *pH*) were carried out at a *pH* of 5.5. For each experiment (except otherwise stated), 0.5 g of adsorbent was measured and put into a 250-mL screw cap conical flask containing 20 mL of the Pb(II) ions at the desired concentration which ranged between 10 and 120 ppm in this study. After agitating the solution for a predetermined time interval (20-120 minutes) with a magnetic agitator, samples were then filtered using filtered paper (Watman N° 1), thus separating the solid/adsorbent from the liquid/solution phase. The filtered solution was put into test tubes containing dithizone and ammoniacal buffer solutions to form complexes. The concentration of the residual Pb(II) ions were determined spectrometrically using a UV-visible spectrophotometer CORNING6259 at λ_{max} = 490 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:

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

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

2.4 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.

2.4.1 Pseudo-first-order model

This model is based on the assumption that the adsorption rate is proportional to the number of available sites [33] and is calculated by the following equation:

$$dQ_t/dt = K_f(Q_e - Q_t) \tag{3}$$

Where Q_t and Q_e (mg/g) are the amounts of adsorbate retained per unit weight of adsorbent at given time and at equilibrium respectively. K_f (min^{-1}) is the rate constant of the adsorption process.
By integrating between $t=0$ and $t=t$, we obtain the following:

$$\ln(Q_e - Q_t) = \ln Q_e - K_f\, t \tag{4}$$

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

2.4.2 Pseudo-second-order model

It is based on the assumption that adsorption rate is proportional to the square of the number of unoccupied sites [34]:

$$dQ_t/dt = K_s(Q_e - Q_t)^2 \tag{5}$$

where K_s (g.mg^{-1}.min^{-1}) is the rate constant for the pseudo-second order adsorption. By integrating between $t=0$ and $t=t$, we obtain the following:

$$t/Q_t = 1/K_s Q_e^2 + t/Q_e \tag{6}$$

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.

2.4.3 Elovich model

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

$$dQ_t/dt = \alpha \exp^{-\beta Q t} \tag{7}$$

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

By integrating between $t=0$ and $t=t$ we obtain the following after some simplifications

(assuming $\alpha\beta t >> 1$):

$$Q_t = [\ln(\alpha\beta) + \ln t]/\beta \tag{8}$$

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

2.4.4 Intra-particle diffusion model

The intra-particle diffusion model equation can be written as follows [35]:

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

where K_{id} is the inter-particle rate constant ($mg.g^{-1}.min^{-1/2}$) and C is the intercept. By plotting $Q_t(mg.g^{-1})$ 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 [35].

2.5 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.

2.5.1 The Langmuir isotherm

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

$$Q/Q_m = KC_e/(1+KC_e) \tag{10}$$

In this equation Ce 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:

$$C_e/Q = 1/K.Q_m + C_e/Q_m \tag{11}$$

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

2.5.2 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]:

$$Q = K_d C_e^{1/n} \tag{12}$$

In this equation, Q is the amount adsorbed at the surface; Ce 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:

$$\ln Q = 1/n \ln C_e + \ln K_d \tag{13}$$

From which we see that a plot of ln Q versus ln C_e should result in 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:

2.5.3 Temkin isotherm

It is expressed in linear form by the following relationship between the amount adsorbed and concentration in solution [36]:

$$Q_e = B(\ln K_T + \ln C_e) \tag{14}$$

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 [37].

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 Figs. 1 and 2 below.

The analysis of the first spectrum (Fig. 1) show absorption bands at 3688 cm^{-1}; 3648 cm^{-1}; and 3618 cm^{-1} which correspond to stretching vibrations of the hydroxyl (OH) group of KAO and water, and average band at 1114 cm^{-1} by the Si-O functional group and at 1000, 1025, 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. Another band between 790-748 cm^{-1} can be seen as well, which is a translational vibration band for Si-O-Al. Finally a Si-O-Si characteristic band at 666 cm^{-1} in KAO.
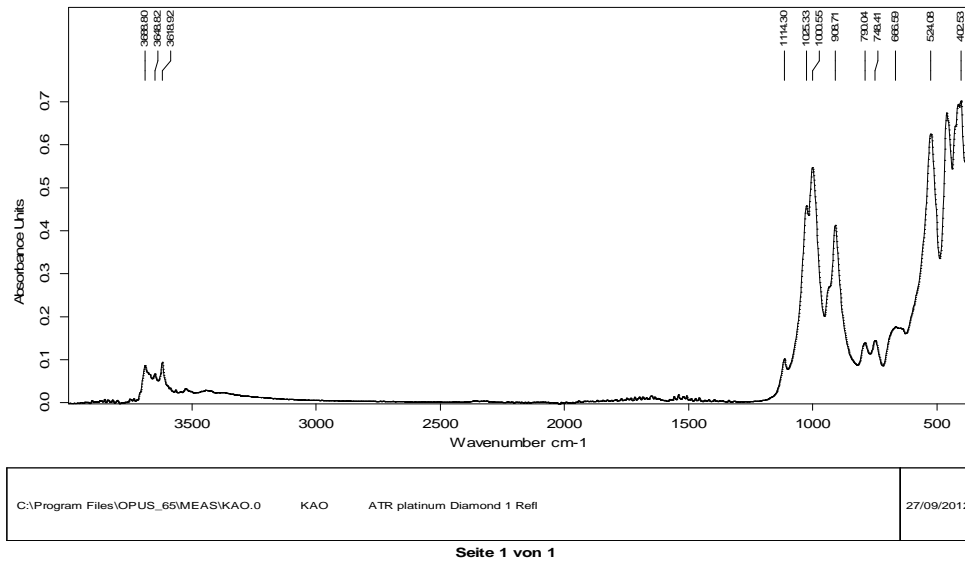
Fig. 1. IR spectra of Kaolinite on platinium in KBr matrix

We observe the second spectrum (Fig. 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} , and for Si-O-Al at 787 cm^{-1} and 542 cm^{-1} are present.

3.2 Effect of Contact Time

Fig. 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$_o$= 60 mg/L) with 0.5 g of adsorbent (KAO and MET) at 27 ºC. The contact time ranged between 20-120 minutes. The uptake of Pb(II) ions onto the adsorbents nearly reached equilibrium after 30 minutes. Based on these results, it was considered as the equilibrium time throughout our study. It is inferred from this figure that for the same contact time and adsorbent dose, KAO shows a higher adsorption potential (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 both KAO and MET). The enhanced adsorption of lead (II) ions with increase in contact time has been explained as due to the decrease in boundary layer resistance to mass transfer in the bulk solution and an increase in the kinetic energy of hydrated ions [10]. By increasing the contact time, the boundary layer resistance will be reduced and there will be an increase in the mobility of ions in the solution.
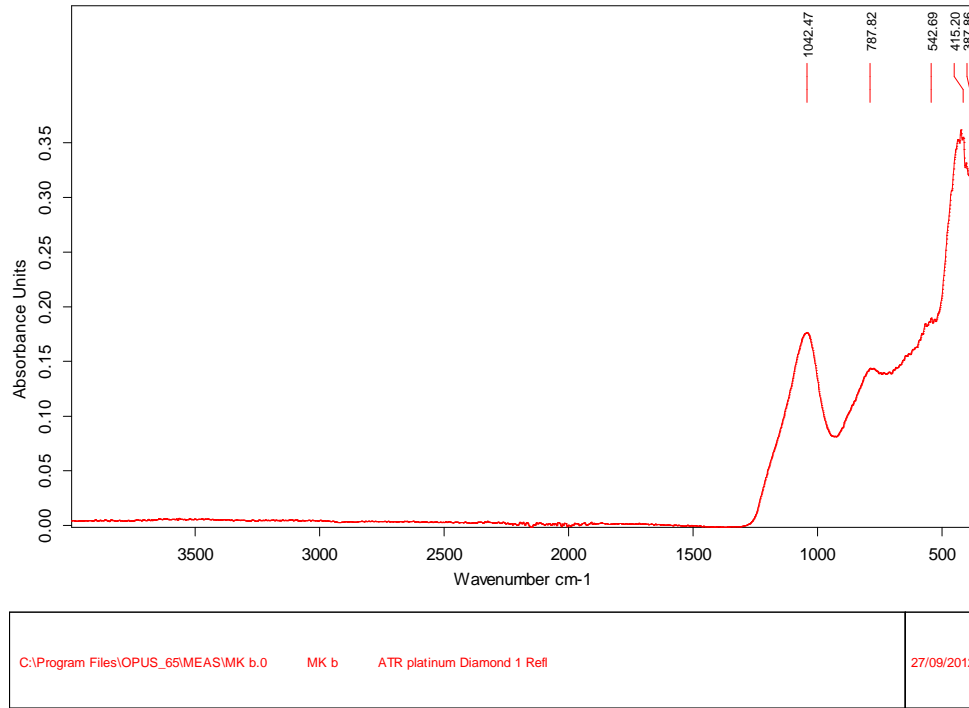
Fig. 2. IR spectrum of metakaolinite on platinium film inside KBr matrix

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 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 (Fig. 4) is the fact that more than 80% removal of Pb(II) ions for both KAO and MET were obtained just for adsorbent weights ranging between 0.1-0.2 g. The adsorption capacity of the adsorbents (that is, the Pb(II) ion removal) is higher at the beginning, most likely 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.
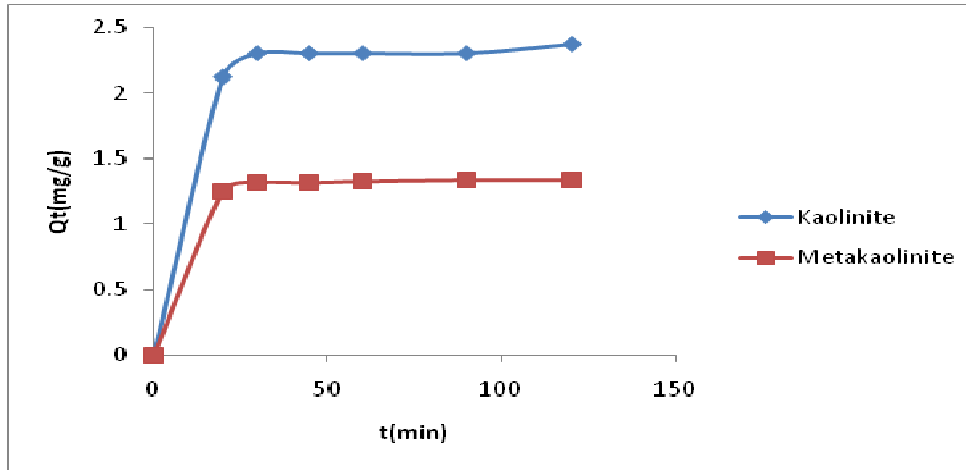
Fig. 3. Effect of contact time on the adsorption of Pb(II) ions
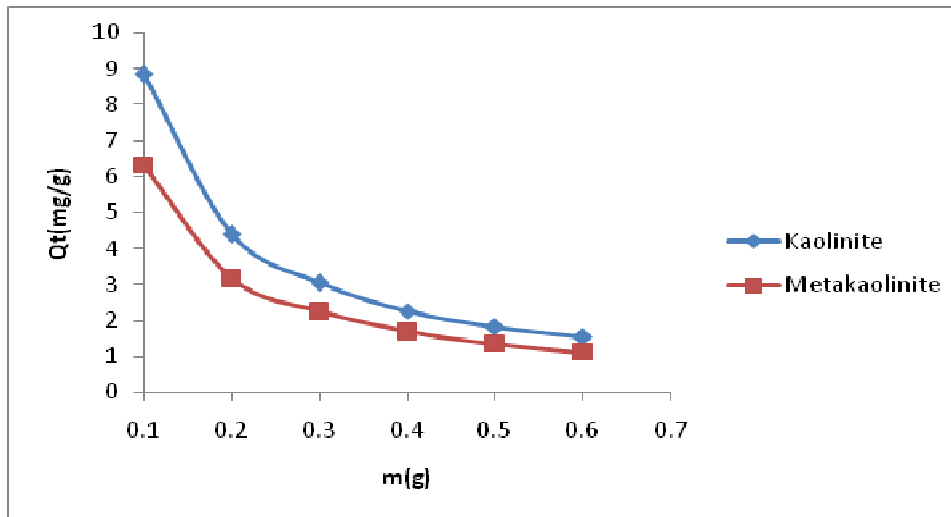*(Conditions: 20mL, 60mg/L Pb(II) solution ; 0.5g KAO , 0.5g MET)*

Fig. 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 ⁰C for a duration of 30 minutes.

The outcome of this set of experiments (Fig. 5) show that the quantity of Pb(II) ions adsorbed changes from 5.85 mg/g to 9.30 mg/g for KAO and 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 increased collision probabilities as the concentration increases. The increase in sorbent capacity with increasing initial Pb(II) ion concentrations may also be due to a higher interaction between substituted Lead (II) and sorbent [10]. 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.
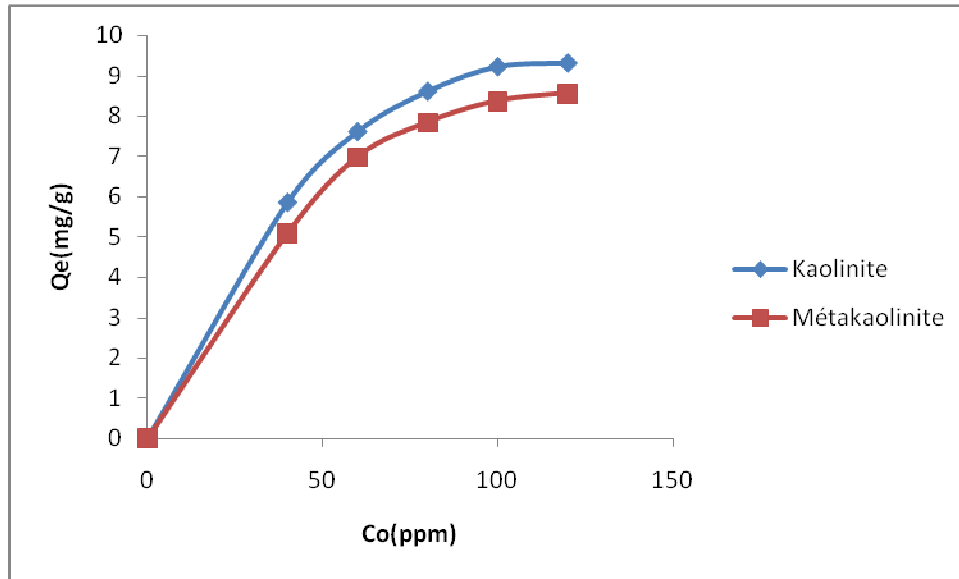

Fig. 5. Influence of Pb(II) ion initial concentration on its adsorption on KAO and MET *(conditions: 0.1g KAO and 0.1g MET, 20mL Pb(II) solution, 30min for KAO and MET, pH 5.5)*

3.5 Effect of *pH*

Fig. 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 HNO$_3$ 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 a slight increase in adsorption of Pb(II) ions as the solution *pH* passes from 2.5 towards 7. In the case of KAO, the quantity adsorbed falls slightly at low acidic *pH* value 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 significant 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 [38] and decreases slightly thereafter. So, for further experiments *pH* was maintained at 5.5 throughout.
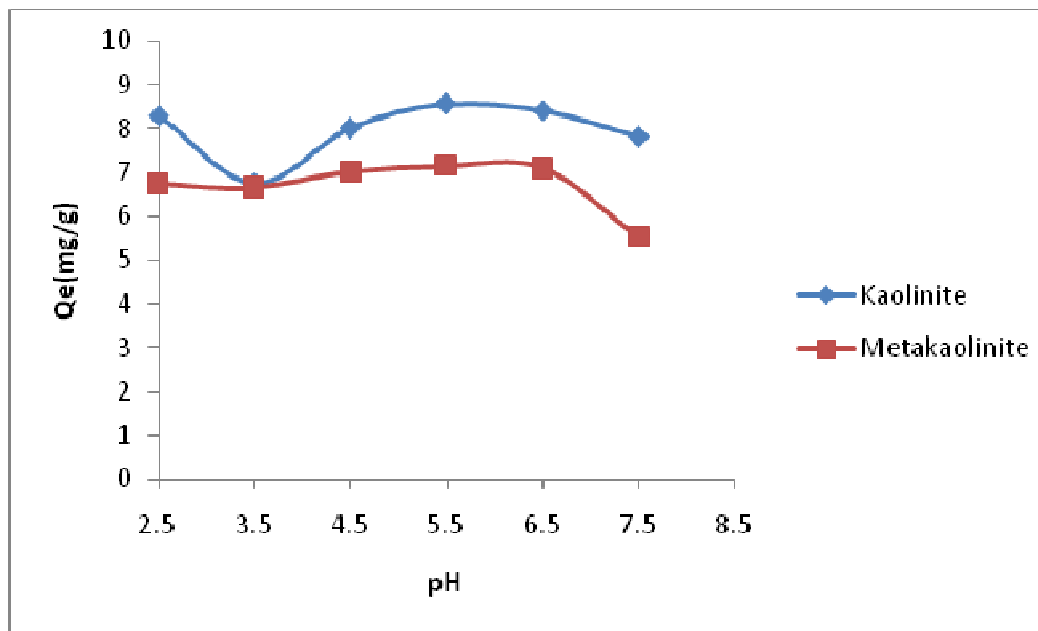
Fig. 6. Effect of *pH* of Pb(II) solution *on adsorption*
(conditions: 20mL, 60mg/L Pb (II) solution ; 0.1g KAO, 0.1g MET, t_e=30 min,for KAO and MET)

3.6 Adsorption Kinetics

Adsoption 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. Figs. 7 and 8 show some linear relationships between adsorbed quantities and time while the characteristic parameters are given in 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 a high correlation coefficient (around 0.999), therefore suggesting that the rate is limited by chemisorption. The general explanations for Elovich model with r^2 greater than those of pseudo-first order and intra particle diffusion, involve a variation of the energetic of chemisorption with the heterogeneous active sites. This supposes that the heterogeneous sorption mechanism is likely to be responsible for the uptake of Pb(II) ions. Elovich model basically supports chemisorption. Different kinetic behaviors for each adsorbent are a result of the structural differences that exist between them [13]. Low correlation coefficients and gradients obtained with the inter-particle diffusion model means that this model does not describe KAO and MET adsorbents well. This result indicates that Pb(II) ions slowly diffuse into the pores of the different adsorbents and therefore constitute a limiting step [39].
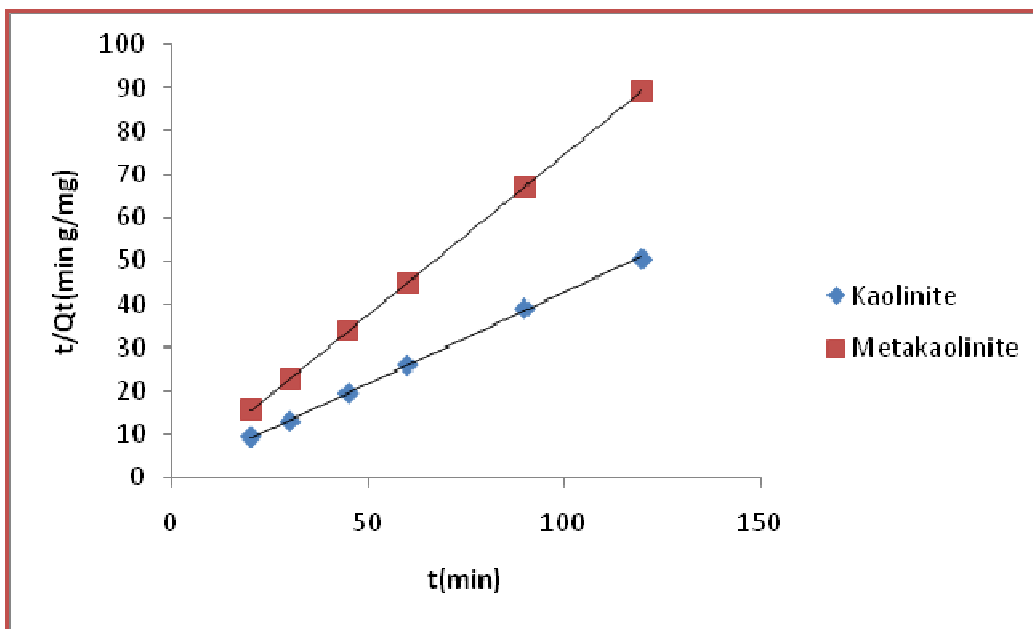
Fig. 7. Linear transformation of second order kinetic model at 60mg/L and pH 5.5
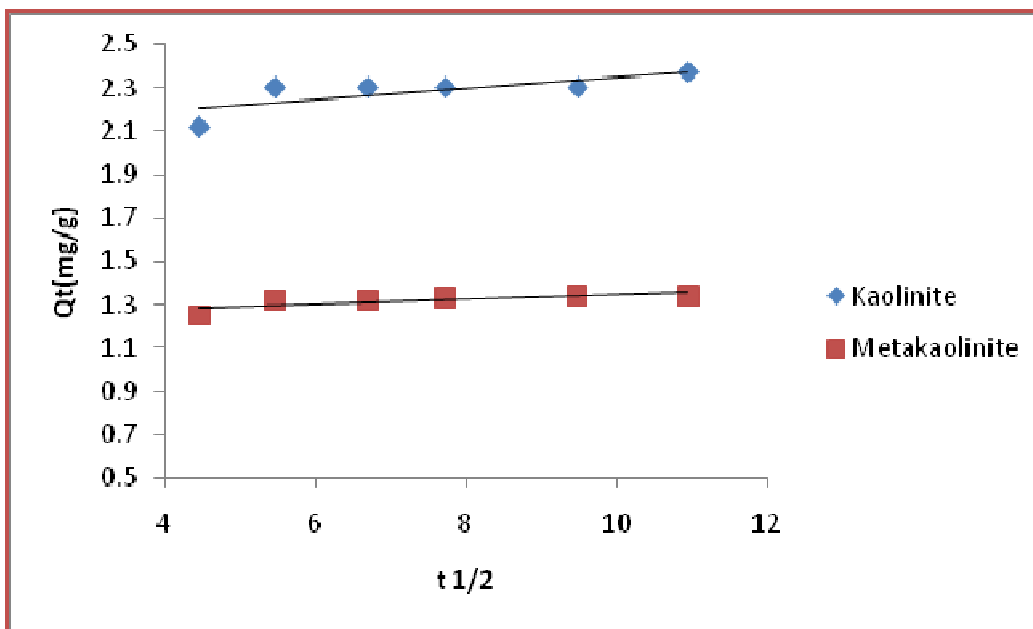

Fig. 8. Linear transformation of intra-particle diffusion model at 60mg/L at pH 5.5

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

Adsorbent		KAO	MET
C_o(mg/L)		60 ppm	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
	$r2$	0.583	0.608

3.7 Adsorption Isotherms

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 (Fig. 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. In addition, we can conclude that adsorption is also favorable by the Freundlich isotherms, (Fig. 10), since $0<1/n<1$ in both cases of adsorbents. In Table 2 the results of the Temkin isotherm are also given (Fig. 11). We deduce that the adsorption energy variation B_T is positive (endothermic reaction) both for KAO and MET [40]. Given that the values of B_T are all less than 8kJ/mol, the interactions 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 (Table 2 below), 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 by Pb(II) ions on the outer surface of the adsorbents, and translates to a decrease in attraction between the adsorbent surface and Pb(II) ions with increases in separation distance [41]. The fact that the Langmuir model best fits the experimental data may be due to the homogenous distribution of active sites on the adsorbent surfaces since the Langmuir equation assumes surface homogeneity.
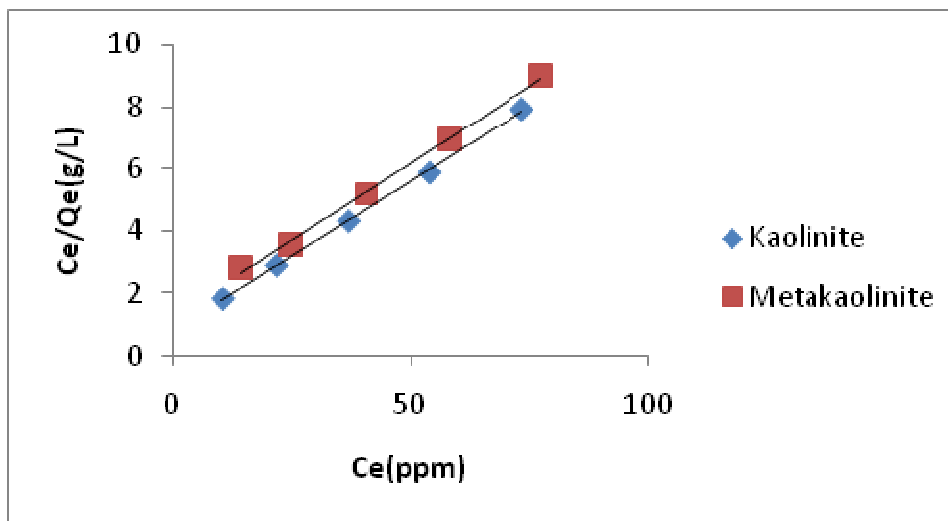
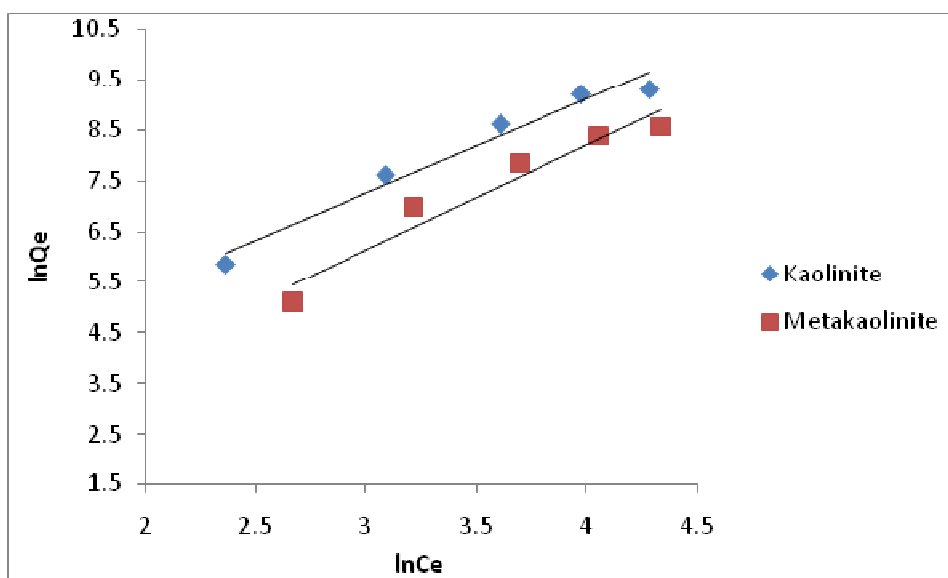**Fig. 9. Linear transformation of Langmuir isotherm**

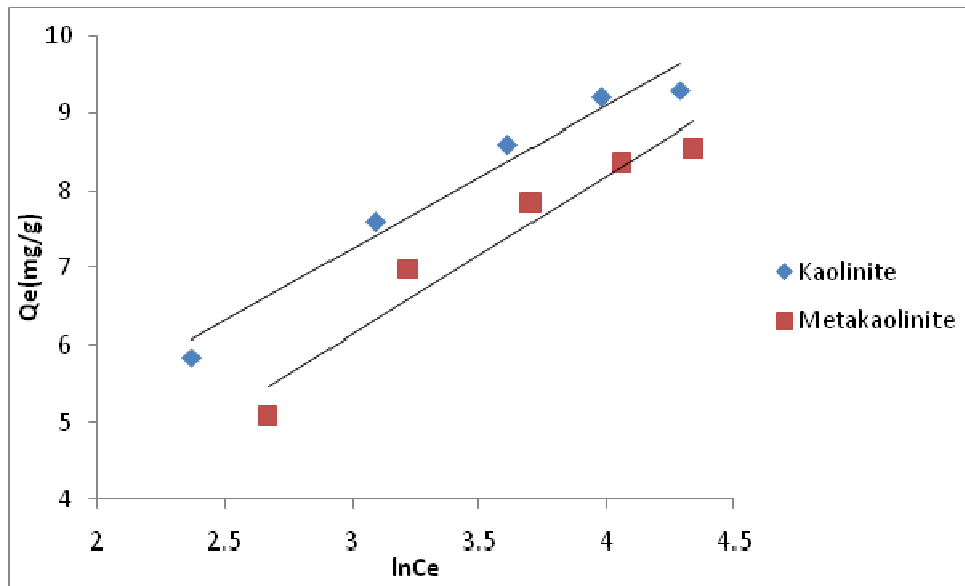**Fig. 10. Linear transformation of Freundlich isotherm**

Fig. 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 in Table 3 below. All the values are less than unity in the range of concentrations tested in this study, implying that the 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 evaluate some southern Cameroonian clays 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 sorption of Pb(II) ions onto KAO and MET is not very much dependent on *pH* in the range 2.5 - 5.5. 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. On Table 4 below is displayed the adsorption capacity of other materials as compared to those obtained in this work. 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 and others from diverse origins [18,30,32].

Table 4. Comparison of the quantity of Pb adsorbed by different adsorbents

Author	adsorbent	Maximum adsorption capacity (mg/g)
[18]	Natural and synthetic Calcite	200mg/g and 150mg/g
[30]	Multiwalled carbon nanotubes	29.71 mg/g for MWCNTs/PAAM without HA and 37.44 mg/g for the (MWCNTs/PAAM_HA)
[32]	Few-layered graphene oxide	842 mg/g
This work	KAO	2.37 mg/g
This work	MET	1.34 mg/g

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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