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Optimization of the Adsorption of Heavy Metals (Copper, Lead) in Aqueous Solution by the Fine Sodium Fraction of Loukolela Clay

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Abstract: *Objective:* The general objective of this work is to study the adsorption capacity of two heavy metals (Pb^{2+}, Cu^{2+}) by the fine sodic fraction of the clay collected in the locality of Loukoléla. *Materials and Methods:* The kinetics of adsorption allowed us to find a time of equilibrium of copper, lead with the mont-Na. The influence of the pH was carried out in basic and acid medium, the adsorption isotherm is obtained by drawing the curve of the adsorbed quantities according to the concentration at the equilibrium, the Langmuir isotherm was used to write the adsorption of copper and lead. *Results:* The equilibrium time is reached at t =20 min with an adsorption quantity of 64 mg/g for Cu^{2+}; for the Pb^{2+} ion the equilibrium is reached after 25 minutes with an adsorption quantity of 43.2 mg/g of fixed metal. Two models were used for the modelling of this work, namely the Langmuir model and the Freudlich model. This study shows that the Langmuir model gives better results than the Freundlich model with a maximum adsorption capacity of the monolayer of 653.12 mg/g for Cu^{2+} and 100.388 mg/g for Pb^{2+}, Loukoléla clay shows high affinities with copper particles compared to lead particles. These results show that Loukoléla clay can be used as an adsorbent for metallic pollutants.

Keywords: Adsorption Kinetics, Heavy Metals, Clay

1. Introduction

The various human activities such as industrial, agricultural, and other activities generate by-products and wastes that can end up in the environment and compromise the balance of ecosystems. Among these by-products, we find heavy metals that present nuisances even when they are discharged in very small quantities because their toxicity develops by bioaccumulation [1]. Heavy metals in water can come from mining effluents, domestic activities, industrial activities and atmospheric sources [2]. However, industry remains responsible for almost all releases of metals in their various forms to water. There are several methods to remove heavy metals from wastewater, such as chemical precipitation, oxidation, hydrolysis, ion exchange, neutralization, electrochemical remediation, adsorption [3]. Adsorption remains a popular and very effective method for the removal of heavy metals from wastewater [4]. The treatment by the adsorption technique is more used for its efficiency in the abatement of inorganic micropollutants, involving solid-liquid interactions. Moreover, smectite type clays have shown the ability to fix important quantities of metallic trace elements from solutions [1-6]. The Republic of

Congo, whose richness in water resources is obvious, has not yet developed a complete inventory of its drinking water quality, because physicochemical studies of drinking water in some areas of Brazzaville have revealed the presence of trace elements at levels higher than those recommended by the World Health Organization [7-8]. It has been reported in the literature that water can be treated by clay. Several studies have been carried out on Congolese clays, notably in the field of characterization [9-11]. Among these studies, the characterization of the clay of the locality of Loukoléla was revealed to be predominantly montmorillonite with a cationic exchange capacity of 47.38 meq/100g, and this clay has already been applied in the adsorption of organic matter [12, 13]. It is in this perspective that we propose to use the clay of Loukoléla in the adsorption of metals in water precisely the particles of copper and lead.

2. Material and Methods

2.1. Presentation of the Clay Material

The clay material used in this work comes from the locality of Loukoléla. The soil sample was taken at a depth of 50 cm. At the time of sampling, the clay was green in color with a very sticky and plastic consistency. After air drying in the laboratory, the sample was subjected to several operations. The results of the physico-chemical and mineralogical characterization are reported in Table 1. Table 1 presents the characteristics of the modified Loukoléla clay.

Table 1. *Characteristics of the raw clay [12].*

Analyses performed		Results
DRX		**Preponderant mineral: Montmorillonite**
C.E.C		$47,38\ meq/100\ g$
Total specific surface	S.S.E	$58,5\ \text{m}^2/\text{g}$
	S.S.I	$35,4\ \text{m}^2/\text{g}$
Limits of Atterberg	W_L	80,3%
	W_P	40,7%
	$I_P = W_L - W_P$	39,6%
Chemical analysis	SiO_2	52,09%
	Al_2O_3	18,02%
	Fe_2O_3	5,38%
	CaO	0,47%
	M.O	$1,37\ g/kg$
	C.O	$0,99 g/kg$

2.2. Characteristic of the Apparatus

The UV-Visible spectrophotometer we used is a Zuzzi 4211/50 model which allows to measure absorbance in the wavelength range from 200 nm to 1000 nm.

2.3. Preparation of the Sodium Fine Fraction

The fine fraction of montmorillonite obtained by the sedimentometry method was put in sodium form by ion exchange by contact with a 50 mL volume of a 0.5M NaCl solution. The whole was put under agitation for 4h (to release the interleaf cations). After decantation, the interfering chloride ions were removed by washing with distilled water.

The pellet obtained was dried at 100°C and ground, thus obtaining a fine sodium fraction.

2.4. Absorption Spectrum of Copper and Lead

The metallic solution (stock solution) of copper and lead of concentration 5.10^{-2} mol/L each was determined with a spectrophotometer in order to measure the absorbances. The maximum wavelength was obtained by scanning between 350 nm and 1000 nm. Plastic cuvettes of 1 cm optical path were used. Figure 1 shows the adsorption spectrum of copper:
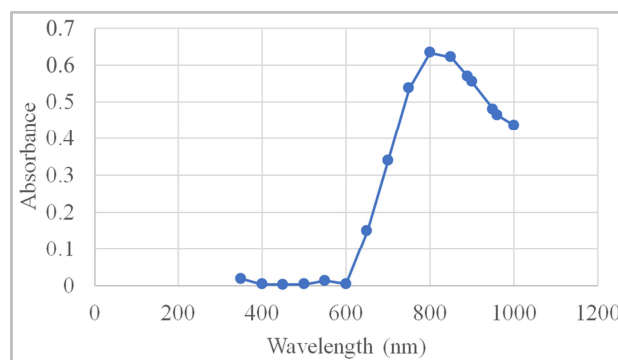
Figure 1. *Absorption spectrum of copper.*

The observation of this curve shows us that the maximum wavelength is reached at 800 nm corresponding to an absorbance A= 0.634. Figure 2 gives us the adsorption spectrum of Lead:
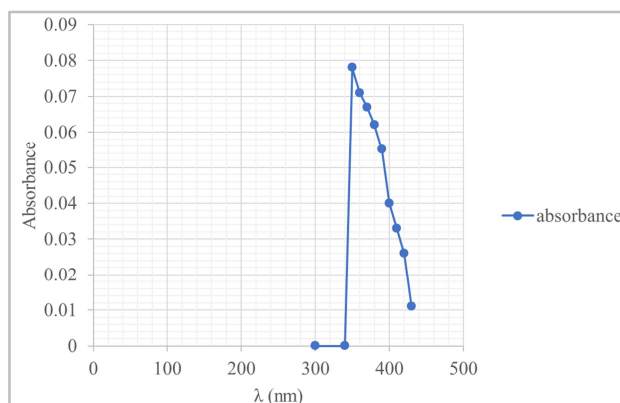
Figure 2. *Absorption spectrum of lead.*

The observation of this curve shows us that the maximum wavelength is reached at $\lambda m_{ax} = 350$ nm corresponding to an absorbance A= 0.634. According to the above curve, the wavelength at the absorption maximum corresponding to the highest value of the absorbance is A = 0.079.

2.5. Adsorption Kinetics of Copper and Lead

Adsorption kinetics is defined by the evolution of the adsorbed amount as a function of the adsorbent/adsorbate contact time.

The amount of solute adsorbed is calculated using the equation:

$$Q_t = \frac{(C_0 - C_t)}{m} \times V; \quad C_t = \frac{DO_e \times C_0}{DO_i}$$

With: C_0: initial concentration in mg/l; Ce: concentration of the supernatant at equilibrium in mg/l; C_t: concentration of the supernatant at time t in mg/l.

m: mass of clay introduced in g; V: total volume of the sample in L.

Q_t: Quantity of pollutant adsorbed per unit mass of clay at the time t in mg/g.

ODe: Optical density or absorbance measured at equilibrium

ODi: Initial optical density or absorbance of the initial solution.

Our study consists in observing the quantities of Cu^{2+} and Pb^{2+} ions fixed by the Na-mount as a function of the contact time between the clay and the aqueous metal solution and to determine the equilibrium time.

2.5.1. Adsorption Kinetics of Copper and Lead by Na-Mount

The influence of time was studied in the range of 5-40 min. The tests were performed on mixtures of 0.5 ml of the aqueous solution containing Cu^{2+} ions of concentration 3.10^{-2} mol/L, under magnetic stirring for 4 min, with a mass of 0.05 g of adsorbent (mont-Na) in a 50 ml beaker at room temperature. At the end of each fixed time the solid and liquid phases are separated by centrifugation for 30 min at 4000 rpm. The liquid phase obtained is first filtered with a filter paper and then the recovered filtrate is analyzed with a spectophometer.

2.5.2. pH Effect

The adsorption experiments, on activated clay, are performed to determine the adsorption capacity of the metal (copper) by the fine sodium fraction. The pH effect was studied using a pH meter. Samples of mass 0.05 g of Na-mount were mixed with 0.5 ml of aqueous solution containing either Cu^{2+} ions or Pb^{2+} ions of concentration 3.10^{-2} mol/L, under magnetic stirring in a 50 ml beaker. The pH of the solutions was adjusted to the following values: 2, 4, 6, 8, 10 and 12 by adding a few drops of HCL (1M) or NAOH (1M) solutions. Then, the obtained mixtures were left to rest according to the equilibrium time. At the end of this fixed time, the solid and liquid phases are separated by centrifugation for 30 min at 4000 rpm. The liquid phase obtained is first filtered with a filter paper and then the recovered filtrate is analyzed with a spectrophotometer.

2.5.3. Adsorption Isotherms of Copper and Lead

The adsorption isotherms of copper and lead were studied by preparing dilute solutions from the 3.10^{-2} mol/L solution while remaining in the concentration range of the calibration curve. Mass samples of 0.05g of Na-mount were mixed with 0.5ml of aqueous solution containing Cu^{2+} or Pb^{2+} ions of varying concentration (0.0045; 0.0075; 0.0114; 0.015; 0.0189) mol/L under magnetic stirring in a 50ml beaker according to a set pH. The pH of the solutions was adjusted by adding a few drops of HCL (1M) or NAOH (1M) solutions. Then, the obtained mixtures were left to rest according to the equilibrium time. At the end of this fixed time, the solid and liquid phases are separated by centrifugation for 30 min at 4000 rpm. The liquid phase obtained is first filtered with the filter paper and then the recovered filtrate is analyzed by spectrophotometer.

3. Results and Discussion

3.1. Kinetics of Copper Adsorption by Na-Mount

The figure below shows the results of the amounts of copper adsorbed by mont-Na as a function of contact time.
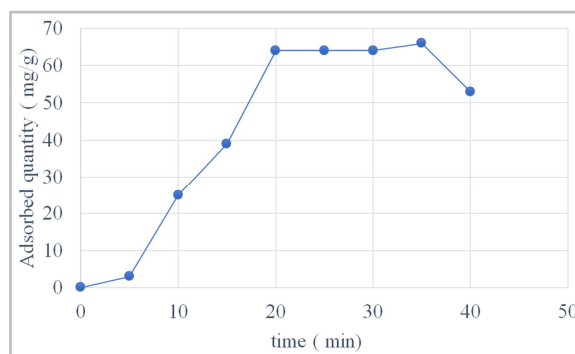

Figure 3. Kinetics of copper adsorption by Na-mount.

The observation of the above figure shows that the adsorption of copper by Na-mount can be decomposed into three phases: a first one very fast, followed by a second one of medium speed to reach the saturation level and a third phase showing a decrease of the adsorption quantity. The first stage is explained by the existence of easily accessible adsorption sites, followed by a diffusion towards less accessible adsorption sites before reaching an adsorption equilibrium where all sites become occupied. After equilibrium, metal adsorption is not noticed. The rapidity of the retention reactions of the metals copper, zinc, mercury and cadmium by the clays as well as the release (desorption) of the adsorbed ions has been observed by several researchers [14-17]. The equilibrium time is reached at t = 20 min with an adsorption quantity of 64 mg/g correspnding to an adsorption percentage of 12.52%.

3.2. Kinetics of Lead Adsorption by Na-Mount

The figure below shows the results of the amounts of lead adsorbed by mont-Na as a function of contact time.
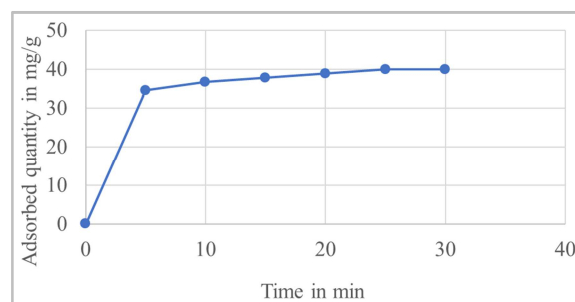

Figure 4. Adsorption kinetics of lead chloride.

We notice a strong adsorption of the metal by the clay from the first 5 minutes of metal-clay contact followed by a slow increase until reaching the equilibrium state. The equilibrium time is 25 minutes of contact between the aqueous phase containing lead and the adsorbent. Other previous studies, carried out on this metal confirm the rapidity of the retention reactions of this element by the clay [18-19]. The kinetics obtained show that the clay is a good adsorbent for lead with an elimination reaching 26.61% with 39.93 mg/g of quantity of the metal fixed.

3.3. Effect of pH

The pH plays an important role in the adsorption. It represents the main parameter that considerably influences the adsorption of metals on clays [18]. Figure 5 shows the evolution of the adsorbed quantities at different pH for copper particles.
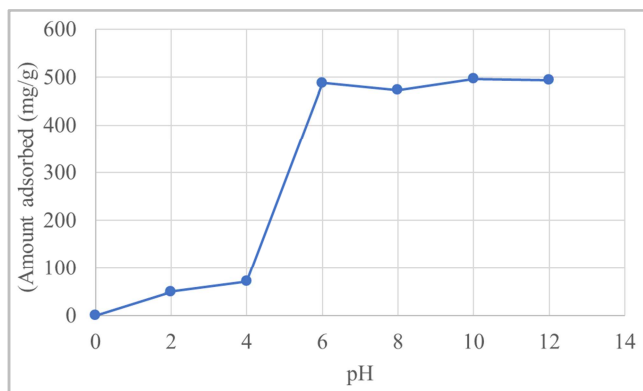

Figure 5. *Effect of pH on the amount of copper adsorbed by mont-Na.*

The observation of this curve presents three parts. The first part corresponds to the pH values from (0 to 4), the second part from (4 to 6) and finally the third part from (6 to 12). The first part gives us low quantities of adsorbed copper, the second part presents us a slope until reaching a plateau. A study on the adsorption of copper at a pH lower than 6 by a clay material was also made, at this pH the clay adsorbs less particles of copper [20]. Indeed, at an acid pH there is an excess of H^+ ions which would compete with the Cu^{2+} ions in solution [20]. The Si-OH groups are more protonated leading to the elimination of the water molecule and leaving only the positive charges on the surface of the clays; this leads to a deficit in the formation of the complex with Cu^{2+} ions [14-21]. At pH above 6, the retention of copper ions increases rapidly, which can be explained by the availability of OH^- ions; the clay surface has become increasingly negatively charged, which probably increases adsorption by electrostatic attraction forces. According to Abollino, at pH > 6, the enhancement of copper adsorption is attributed to the precipitation of copper oxides [21]. From this curve we noticed that the maximum adsorption amount is obtained at pH=10 with an adsorption amount of 497.038 mg/g corresponding to an adsorption percentage of about 97.26%.

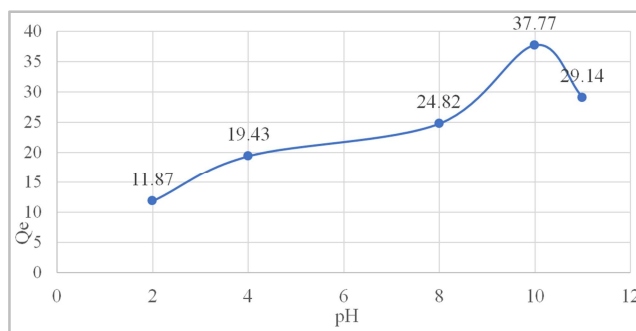Figure 6 below shows the removal of lead at different pH.

Figure 6. *Effect of pH on the adsorption of lead particles.*

The observation of the above figure shows that the adsorption of lead is largely affected by the pH of the medium. In acidic medium the adsorbed quantities are quite low (11.87 and 19.43 mg/g). This can be explained by the fact that in a very acidic environment Pb^{2+} ions adsorb with difficulty on the surface of the clay already saturated by H^+ ions, which are very mobile and insert themselves more rapidly. The adsorption reaches its maximum at pH =10, the adsorbed quantity is 37.77mg/g with a yield of 25.17%. The pH decreases at 11. This decrease may be due to the reduction of negative charges on the surface of the clay which would attract the metal cations. The Pb^{2+} ions are retained on the surface of the clay by coulombic forces.

3.4. Adsorption Isotherms

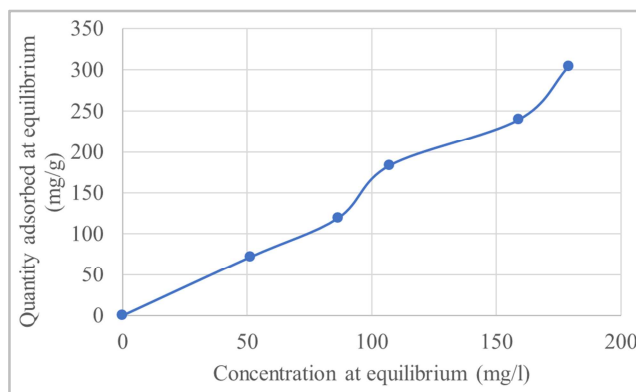The figure below represents the isotherm of adsorption of copper by mont-Na:

Figure 7. *Adsorption isotherm of copper by mont-Na.*

We find that the amount of adsorption increases with the concentration at equilibrium, with a maximum of adsorption at Qads = 304.3068 mg/g; corresponding to a percentage of 94.44%. The isotherm of adsorption of copper by Na-mount, corresponds to the S-type isotherm. This isotherm is met when the molecules of the solute are fixed by the intermediary of only one grouping and when the adsorption of the solute is appreciable. The S isotherm reflects a variable affinity of the adsorbent to the adsorbed substance [22]. Figure 8 below shows the adsorption isotherm for Pb^{2+} ions:
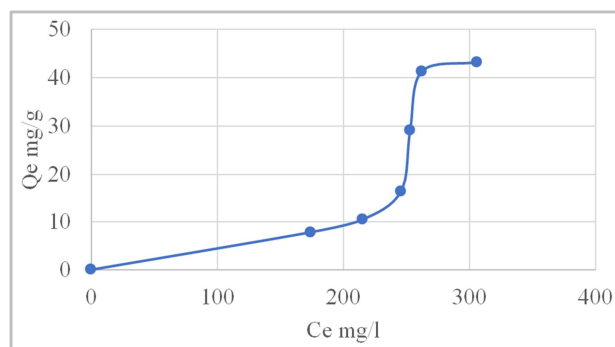
Figure 8. Adsorption isotherm of lead particles.

An increase in the amount of adsorbed Pb^{2+} particles is observed with increasing equilibrium concentration. An adsorption quantity of 43.2 mg/g of metal was fixed. The curve obtained is S-shaped, presenting at low concentration, an upward facing concavity. The adsorbed molecules favor the subsequent adsorption of other molecules (cooperative adsorption). This is due to the molecules attracting each other by Van Der Waals forces, and grouping together in islands in which they pack against each other. This behavior is favored, on the one hand, when the solute molecules are adsorbed vertically as is the case for molecules with a single functional group and on the other hand, when the molecules are in strong adsorption competition with the solvent. For the modeling of the adsorption isotherms obtained, we chose two models, that of Langmuir and Freundlich. This modeling allows us to determine the maximum adsorption capacity of the monolayer and many other parameters.

3.4.1. Langmuir Model of Copper

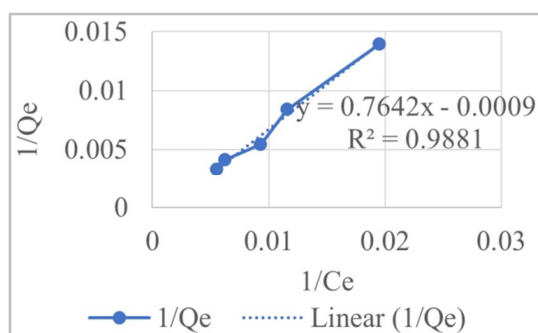The adsorption isotherm of the Langmuir model for copper is represented by figure 9.

Figure 9. Langmuir model for copper.

The line is of the form: y = 0.7642x-0.0009; with a correlation factor $R^2 = 0.9881$. The different parameters of the Langmuir models are summarized in Table 2.

Table 2. Langmuir model parameters.

Parameters	Qmax (mg/g)	K_L (L/mg)	R^2
Mont-Na	653,12	0,004	0,9881

The value of the maximum adsorbed capacity required for the monolayer Qmax = 653.12 mg/g quite high confirms the affinity of copper on the Na-mount.

3.4.2. Freundlich Model of Copper

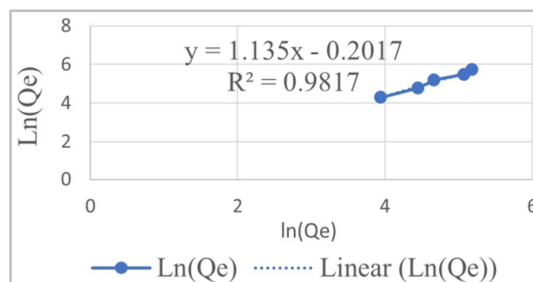The adsorption isotherm of the Freundlich model is shown in Figure 10.

Figure 10. Freundlich model for copper.

The line is of the form: y = 1.135x-0.2017, with a correlation factor $R^2 = 0.9817$.

The different parameters of the Freundlich models are summarized in Table 3.

Table 3. Different parameters of the Freundlich models.

Parameters	1/n	K_F	R^2
Mont-Na	1,15	0,76	0,9817

The parameter n = 0.86; this value is less than 1 which means that the adsorption is low; the adsorption capacity KF=0.76 being lower also indicates low adsorption [23].

3.4.3. Langmuir Model of Lead

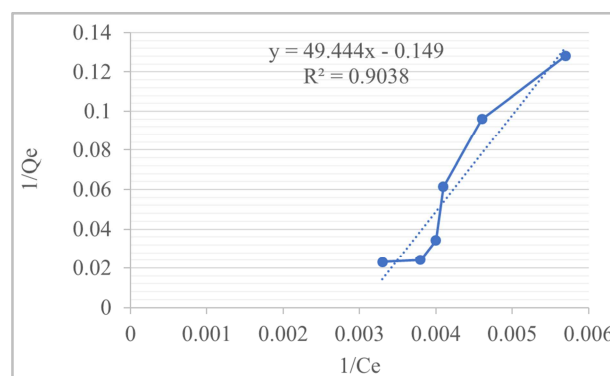The adsorption isotherm of the Langmuir model for lead is shown in Figure 11.

Figure 11. Langmuir model of lead.

The line is of the form: y = 49.444x-0.149, with a correlation factor $R^2 = 0.9038$. The different coefficients determined from this line are grouped in Table 4.

Table 4. Different Langmuir coefficients.

Q_m	K_L	R^2
$1,388.10^2$	$1,584.10^{-2}$	0,9038

3.4.4. Freundlich Model of Lead

The adsorption isotherm of the Freundlich model of lead is shown in Figure 12.

The different parameters of the Freundlich models are summarized in Table 5.
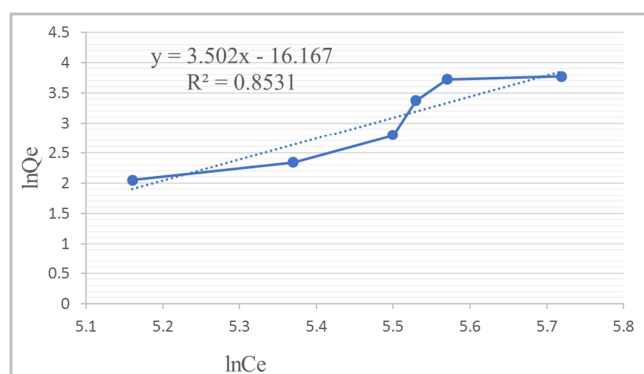
Figure 12. *Freundlich model of lead.*

Table 5. *Different Freundlich coefficients.*

1/n	K_F	R^2
3,502	$9,52.10^{-8}$	0,8531

In view of all the above, the Langmuir model gives better results than the Freundlich model. It is therefore preferable for this study to use the Langmuir model.

4. Conclusion

The objective of our work was to evaluate the adsorption capacity of the fine sodium fraction obtained from Loukolela clay on copper and lead particles. To achieve this objective several methods were used. The kinetics of adsorption allowed us to find a time of equilibrium of copper, lead with mont-Na. The influence of the pH was realized in basic and acidic medium, the isotherm of adsorption is obtained by drawing the curve of the adsorbed quantities according to the concentration at the equilibrium, the isotherm of Langmuir was used to write the adsorption of copper and lead. The contact time between the Na-mount and the copper particles was obtained at t =10 min and after 25 minutes for lead. The optimal pH is obtained in basic medium corresponding to 10 for both ions (Cu^{2+}, Pb^{2+}). The adsorption isotherm allowed us to deduce an adsorption quantity Qads = 304.3068 mg/g for copper and 43.2mg/g for lead. Two models were used to describe the adsorption of the particles namely the Langmuir model and the Freundlich model, the Langmuir model presents the best results compared to the Freundlich model.

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