

# Adsorptive Removal of Pb(II) and Cd(II) Ions From Aqueous Solutions Onto a Cameroonian Natural Clay

David Dina Joh, Charles Melea Kede, Herve Wembe, Pierre Gerard Tchieta\*  
Bio-organic, Analytical and Structural Chemistry Laboratory,  
Faculty of Science, University of Douala; BP 24157 Douala,  
Cameroon

**Abstract:** The adsorption of Pb<sup>2+</sup> and Cd<sup>2+</sup> ions on clay from the town of Nkongsamba (in the Littoral Region of Cameroon) was carried out to eliminate these two micropollutants in aqueous solution. Mineralogical and chemical analysis carried out onto clay show that it is simply kaolinitic clay with a ratio (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>) greater than 2. From the kinetic study of the phenomenon at room temperature and pH equal to 6.7 the influence of contact time has been highlighted. The influence of the initial concentration of the two cations by setting the contact time, the pH and the temperature shows good retention of Cd<sup>2+</sup> ions compared to that of Pb<sup>2+</sup> ions, while the study of pH gives a maximum retention rate at pH = 6.7. However for the adsorption of the two ions is favoured by low pH values.

**Keywords:** Kaolinitic clay, adsorption, micropollutants, lead, cadmium, contact time, pH.

## 1. INTRODUCTION

The presence of heavy metals in the waters due to industrial waste disposition in the region of Douala (Cameroon), is at the origin of the pollution of surface waters as well as problems encountered during the treatment of drinking water. In terms of the emissions standards [1], which limit the levels of various pollutants of industrial discharge waters at lower rates, it became necessary to implement processes simple and inexpensive, capable of responding to these requirements.

Water pollution is the degradation of the water quality resulting from the introduction of waste due to human activity or natural agents. Thus the pollutants found in the water can be polycyclic organic pollutants (POPs) as polychloride of benzene PCB (waste of transformations in paints and chemical industries) and heavy metals from service stations, household waste, companies and workshops [2]. Heavy metals have a toxicity that destroys the aquatic environment and their accumulation over the food chain could have more or less serious effects on the health of the population by causing cancers, infertility, mortality, and disruption of the endocrine system [3].

However, one special property which characterizes the solid microporous in general and in particular, clays is the ability to adsorb heavy metals and organic substances in aqueous solutions. It would be mainly due to their natural acidity and their high specific surfaces. Its importance is however subject to the influence of several parameters: pH, nature of the

adsorbed element, concentrations. The principle is to set on solid, elements traces metal (ETM), likely to be present in wastewater, which represents a great danger for the environment and human. Their elimination by a simple and inexpensive method has become a necessity in economic terms than that of pollution and growing industry interest. Indeed, in recent years, the law requires the purification of wastewater from of the circuits of washing or cooling of manufacturing facilities [1]. The methods currently used for the purification of waste water are expensive and difficult to apply. There are extraction by emulsion membranes [4], extraction by solvents [5], reverse osmosis [6] and adsorption on activated carbon [7]. The use of the activated carbon which is one of the best treatment, remains hampered by the high price of the adsorbent material. Clay of Nkongsamba (Littoral Region of Cameroon) because of its availability and its abundance is currently used in the industry of ceramics, but its use in depollution, may also be considered in reason for its non-toxicity.

In the present study, the aptitude of Cameroonian clay of Nkongsamba (Littoral Region) in removing heavy metals (lead II and Cadmium II) has been investigated. A series of experiments have been performed to firstly characterize the clay material and secondly the metal adsorption equilibrium onto the clay. For each single metal, the experiments were designed to study the influence of the pH, metal concentration and contact time on the adsorption process in batch system. The adsorption of Pb(II) and Cd(II) at several concentrations with a constant adsorbent dose has been studied in the 2–10 equilibrium pH range at constant temperature. These data have been used in applying adsorption and kinetics model to predict heavy metal adsorption onto the clay, and expressions for the adsorption constants have been obtained.

## 2. EXPERIMENTAL WORK

### 2.1. Materials

The clay used in this work (named NK clay) comes from Nkongsamba which is a town in the Mounjo Division, in the Littoral region of Cameroon. The test site is in the volcanic sub-division of Nkongsamba 1 (District 5) base and is located near the border east of the Douala-Bafoussam highway to 4°56'48 " North latitude and

9°55'47.5" East longitude. The clay material is at first washed several times with distilled and filtered water to eliminate impurities. This material was dried at an oven temperature of 105°C for 24 hours, sieved ( $\Phi \leq 0.002$  mm) and desiccated for characterization experiments and adsorption studies.

Two inorganic salts respectively the crystals of Cadmium Sulfate ( $\text{CdSO}_4$ ) and Lead Nitrate ( $\text{Pb}(\text{NO}_3)_2$ ) from the sale of pharmaceutical and chemical products "Medical management" industry have been dissolved in distilled water to obtain aqueous solutions. Hydrochloric acid HCl and sodium hydroxide NaOH solutions were used for the variation of pH. All glassware were washed in 1N  $\text{HNO}_3$  for 24 hours before use and rinsed with distilled water.

### 2.2. Surface composition and structure determination

The microstructure of the clay surface was studied by using a scanning electron microscope (SEM) and energy dispersive X-ray spectra (EDX). The SEM was used to observe the structure of the clay and the surface components were examined using EDX. The experimental device used consisted of an electron microscope of type FEG QUANTA 450 with an EDX BRUKER QUANTAX EDX system coupled to an SEM microscope with an acceleration of 2 kV. Surface functions were determined by Fourier Transformer infrared spectroscopy (FTIR). The XRD (X ray diffractometry) pattern of the material recorded between 5° and 60° in 2 $\theta$  by intervals of 0.02 s with a count of 10 s has permitted to highlight the solid phases in the presence giving the mineralogical composition of the NK clay. The determination of different oxides and their contents by XRF (X ray fluorescence) completed the determination of the composition of this material.

### 2.3. Batch sorption experiments

50 ml of lead II or cadmium II concentrations ranging from 60 to 150 ppm were mixed with 0.1 g of clay. The Ph were adjusted to the initial concentrations of 2 to 10 using 0.1N HCl and 0.1N NaOH solutions. The samples

were then shaken overnight by magnetic stirrer (400 r/min) at normal room temperature (25°C). For all adsorption isotherm experiments, pH = 6,7± 0,2 were used. After filtering the suspension using 0.2  $\mu\text{m}$  filters, dissolved Pb(II) and Cd(II) concentrations were measured using a Spectroquant Pharo 300 MERCK Atomic Absorption Spectrophotometer (flame and furnace module). The maximum wavelengths were obtained directly by auto scan between 200 and 800 nm. The adsorbed metal concentrations were obtained from the difference between total initial metal concentration and final detected metal concentrations.

For kinetics studies, solutions of 60 ppm (pH = 6.7± 0,2) were used. Aliquots of samples were collected after 20, 40, 60, 80, 90 and 100 min continuously and adsorbed concentrations were measured as previously using Atomic Absorption Spectrophotometer.

## 3. RESULTS AND DISCUSSION

### 3.1. Characteristics of the adsorbent

The SEM was used to observe the surface structure of the clay NK. As shown on Figures 1 and 2, SEM images show that this material has a heterogeneous surface on which there is the presence of the slats. Some pores are also observed on the surfaces of the material. Furthermore, in view of the heterogeneity of the surface of this material, it was necessary to stand out by EDX elementary chemistry composition and by XRF content of different oxides (Figure 3 for EDX results and Table 1 for XRF results) which can influence its adsorptive capacity. Atoms such as silicon, aluminium, magnesium, carbon, gold and iron in different proportions are observed (Figure 3). X fluorescence spectroscopy reveals that the material contains a lot of silica 56.48% characteristic of quartz, 22.39% of alumina who combined with silica can predict the presence of kaolinite, 7.48% characteristic of iron oxide hematite, a value very lower than the threshold of the clays considered as lateritic. The other elements are in trace state. This material is rich in oxides (Table 1).

Electron Image 3

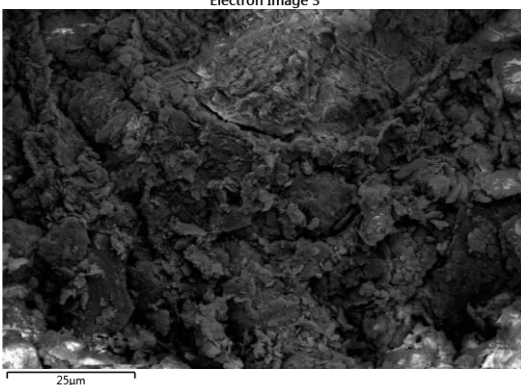


Figure 1: SEM image:electron image

EDS Layered Image 3



Figure 2: EDX layered image

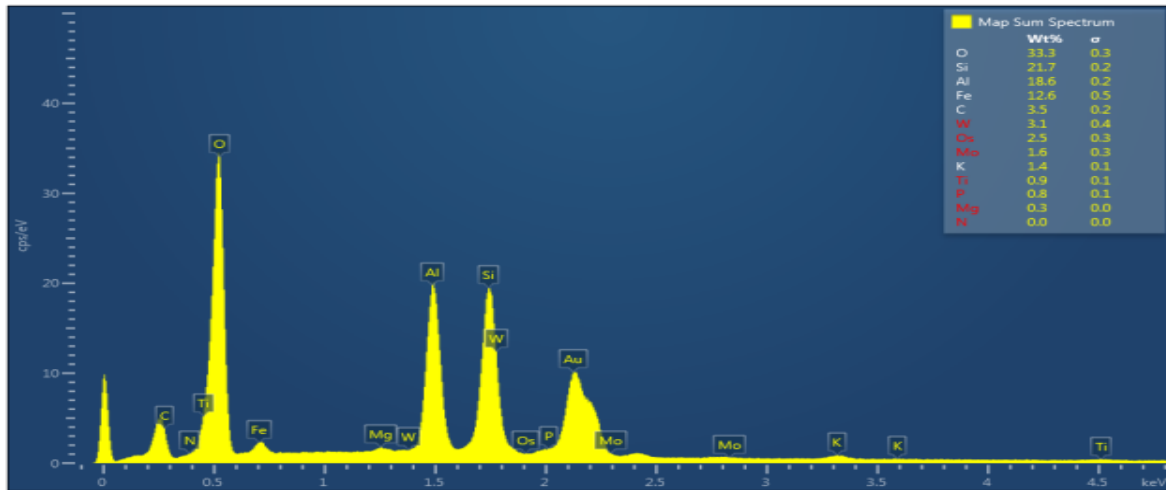


Figure 3: EDX results of NL clay

Table 1: Chemical composition of NK clay

Oxide formula	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	TiO <sub>2</sub>	MgO	P <sub>2</sub> O <sub>5</sub>	ZrO <sub>2</sub>	SO <sub>3</sub>	CaO	Cr <sub>2</sub> O <sub>3</sub>	V <sub>2</sub> O <sub>5</sub>	MnO	SrO	Nb <sub>2</sub> O <sub>5</sub>	Rb <sub>2</sub> O	ZnO	LOI*
Contents%	56.48	22.39	7.48	1.67	1.51	1.48	0.09	0.055	0.03	0.03	0.017	0.016	0.013	0.011	0.008	0.008	0.006	8.64

\*LOI : Lost in ignition

The observation of XRD pattern of the NK clay (Figure 4) shows the significant presence of rays characteristics of kaolinite, quartz and boehmite. The crystalline phase is mainly formed of kaolinite with a value of 79.19%.

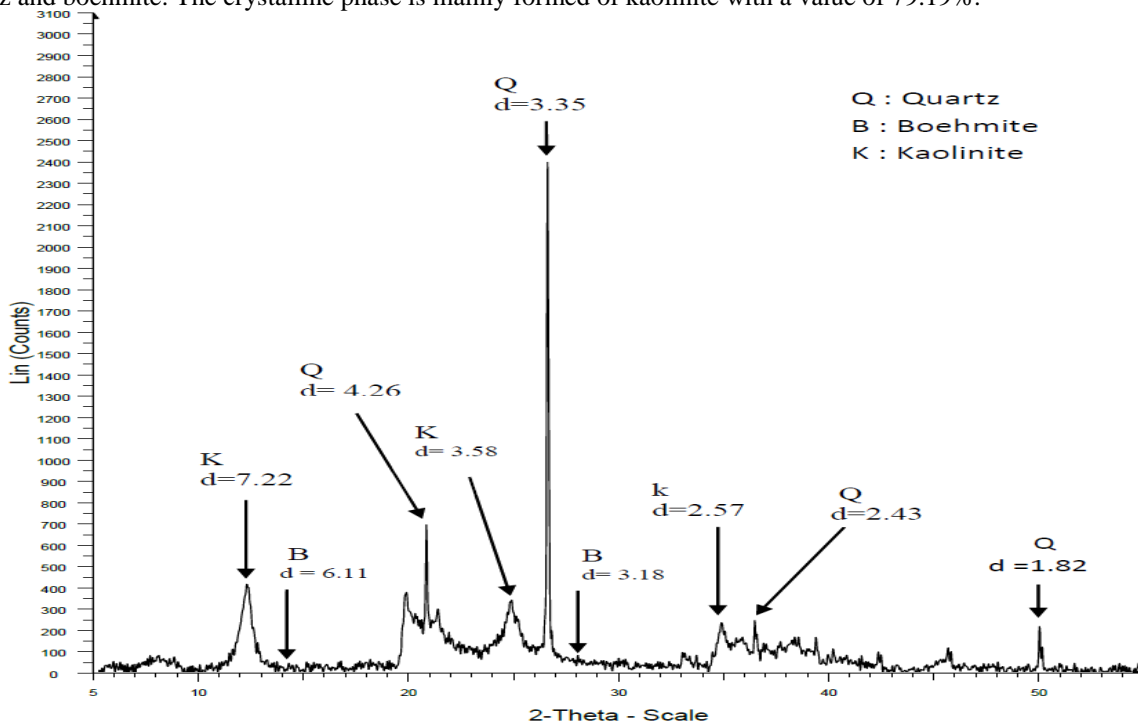


Figure 4: XRD pattern of NK clay recorded between 5° and 60° in 2θ by intervals of 0.02 s with a count of 10 s

The FTIR spectrum of NK clay before adsorption (Figure 5) indicates the presence of predominant peaks at 3692.30 cm<sup>-1</sup>, 3650.96 cm<sup>-1</sup> and 3620.23 cm<sup>-1</sup> (-OH stretching, Al---OH valence vibration and Al---OH interoctahedral vibration), 3363.61 cm<sup>-1</sup> and 3259.21 cm<sup>-1</sup> (-OH stretching), 1637.20 cm<sup>-1</sup> (C=O valence vibration), 1113.88 cm<sup>-1</sup> (Si-O valence vibration), 1025.50 cm<sup>-1</sup> (Si-O-Si, Si-O valence vibration), 997.80 cm<sup>-1</sup>, 908.47 cm<sup>-1</sup> (O-H elongation vibration, Al---OH valence vibration), 791.85

cm<sup>-1</sup>, 747.43 cm<sup>-1</sup> (Si-O, Si-O-Al, (Al, Mg)—OH, Si-O-(Mg, Al) valence vibration), 672.12 cm<sup>-1</sup>, 520.19 cm<sup>-1</sup> (Si-O perpendicular vibration), 456.48 cm<sup>-1</sup>, 421.98 cm<sup>-1</sup> (Al-O-Si, Si-O valence deformation). All functional groups observed such as -OH, C=O, Al---OH, Si—O, (Al,Mg)—OH or (Al,Mg)—OH originally present in NK clay, are available for interaction with the metal ions. Analysis by infrared spectrometry confirms that NK clay is not a laterite.

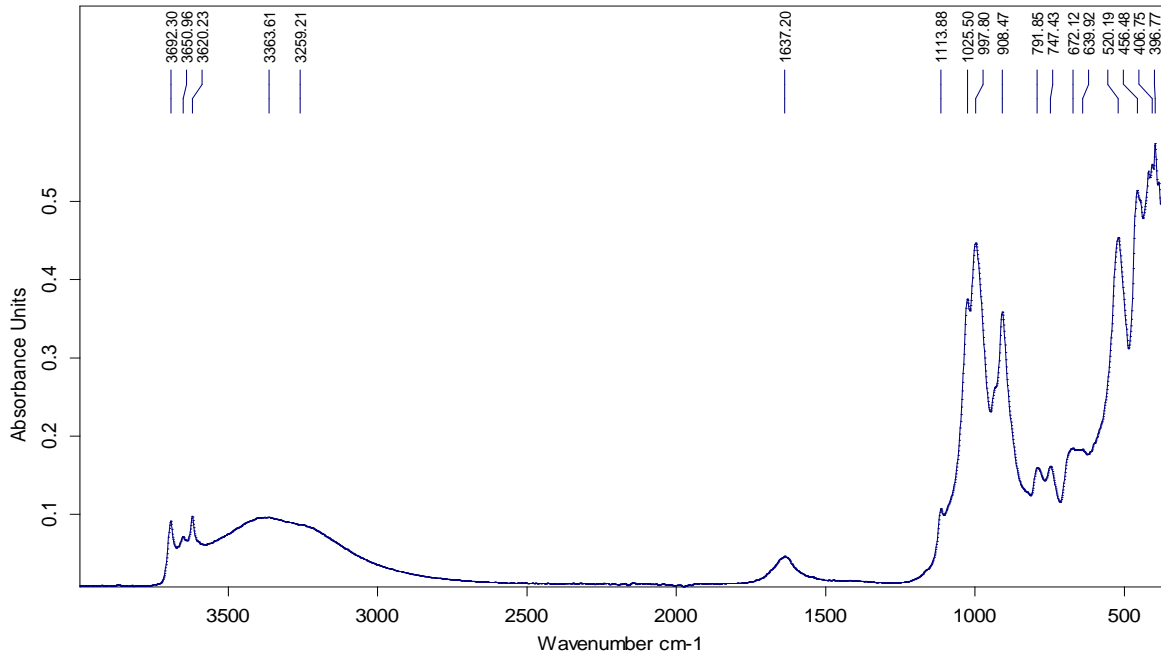


Figure 5: FTIR spectrum of NK clay.

### 3.2. Adsorptions Isotherms-Equilibrium modelling

Analysis of the equilibrium data is important to describe the adsorption process which could be used for design purposes. To obtain the isotherms, initial concentration of Pb(II) and Cd(II) were varied from 60 to 150 ppm while keeping the weight of NK clay, pH and contact time constant. The equilibrium uptake capacity of the NK clay for each metal ion was calculated according to mass balance (equation below):

$$q_e = \left( \frac{C_0 - C_e}{m} \right) \cdot V$$

where  $q_e$  was the amount adsorbed per unit mass of adsorbent ( $\text{mg.g}^{-1}$ ),  $C_0$  and  $C_e$  were, respectively, initial and equilibrium concentrations of metal ion ( $\text{mg.L}^{-1}$ ),  $m$  was the mass of adsorbent (g) and  $V$  was the volume of solution in liters (L).

Adsorptions isotherms are represented on Figure 6. These two curves are similar which indicates that adsorption processes are virtually identical. The shape of the isotherm is of type III characteristic of an adsorbent with wide distributions of sizes of pores with a continuous transition of monolayer adsorption at adsorption in multilayer up to capillary condensation.

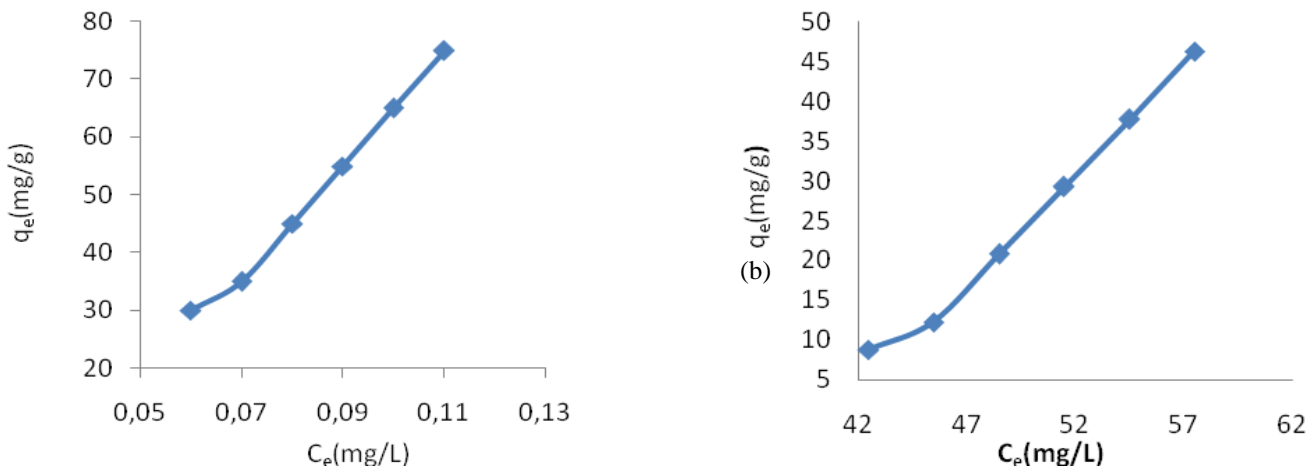


Figure 6: Adsorption Isotherms of cadmium II (a) and lead II (b) on NK clay: room temperature, 0,1 g of clay in 50 mL of solution.

Equilibrium data also permits to develop an equation which accurately represents the adsorption process. Langmuir and Freundlich adsorption isotherms were used to fit the experimental data. The Langmuir isotherm assumes monolayer adsorption whereas the

Freundlich isotherm is an empirical model that is based on sorption on heterogeneous surface. The parameters of Langmuir and Freundlich adsorption isotherms, evaluated from the linear plots (Figures 7 and 8) are presented in Table 2 along with the correlation coefficients.

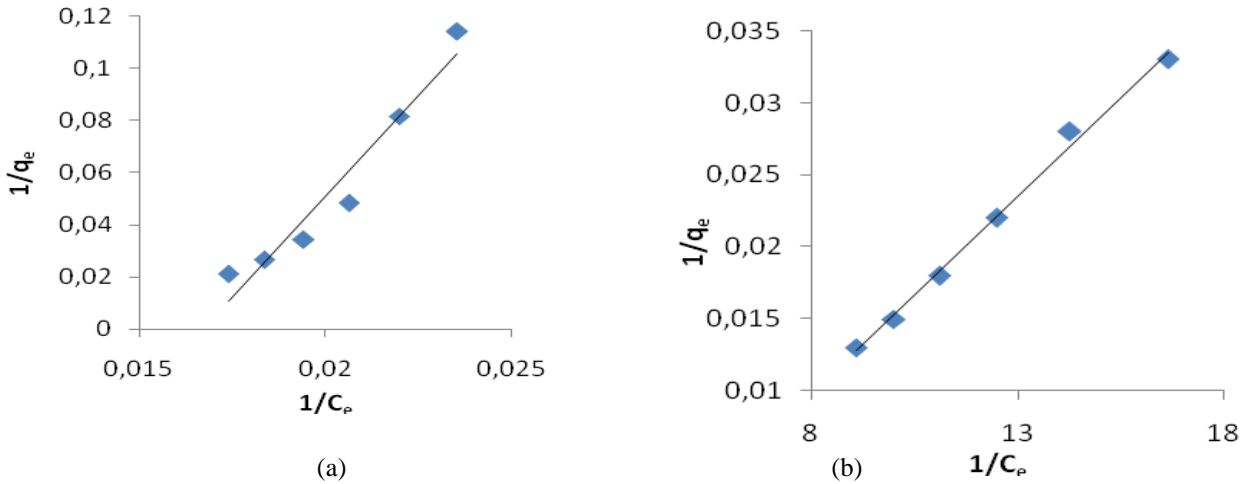


Figure 7: Langmuir Adsorption Isotherm transforms curves of cadmium II (a) and lead II (b) on NK clay: room temperature, 0.1 g of clay in 50 mL of solution.

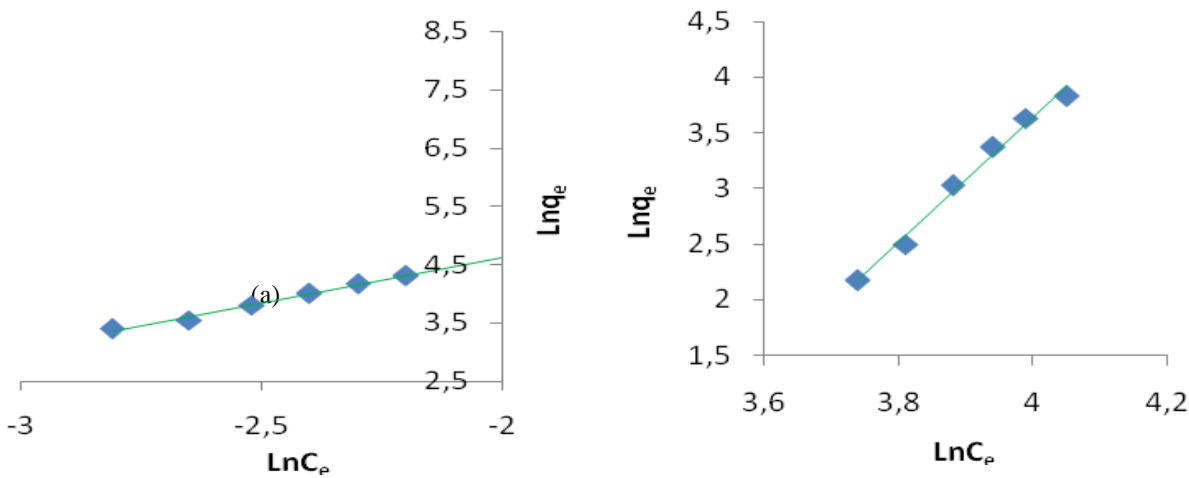


Figure 7: Freundlich Adsorption Isotherm transforms curves of cadmium II (a) and lead II (b) on NK clay: room temperature, 0.1 g of clay in 50 mL of solution.

Table 2: Langmuir and Freundlich constants for the adsorption of Cd(II) and Pb(II) on NK clay

Metal ions	Langmuir constants					Freundlich constants		
	$q_m(\text{mg.g}^{-1})$	$K_L(\text{L}^{-1}.\text{mg})$	$R^2$	$R_{Lmin}(\text{at } 150 \text{ ppm})$	$R_{Lmax}(\text{at } 60 \text{ ppm})$	$K_f$	$n$	$R^2$
Pb(II)	56.60	0.008	0.947	0.418	0.878	1.29	0.113	0.989
Cd(II)	60.34	0.014	0.995	0.257	0.775	1.65	0.148	0.991

With coefficients correlation greater than 0.942, both models are capable of representing the data adequately for the adsorption of the two ions. So much more that  $R_L$  (Langmuir dimensionless factor) values characteristic of adsorption intensity range between 0 and 1 which described a very favourable adsorption in the range of concentrations studied for the two ions.

The magnitude of the Freundlich constants,  $K_f$  (1.29 for Pb(II) ions and 1.65 for Cd(II)) and  $n$  ( $>1$ ) indicate that the uptake of the two ions in the range of studied concentrations from aqueous solutions by NK clay is feasible.

Langmuir constant,  $q_m$ , represents the maximum monolayer adsorption capacity of the adsorbent. The values are  $56.60 \text{ mg.g}^{-1}$  and  $60.34 \text{ mg.g}^{-1}$  for Pb(II) and Cd(II)

respectively. These values are in most cases close or even higher than those observed in the literature on the adsorption of the two ions on clay. Thus,  $q_m$  value was found to be  $11.49 \text{ mg.g}^{-1}$  for the adsorption of lead II ions on Nigerian clay [8], the same values were found to be  $11.59 \text{ mg.g}^{-1}$  and  $11.72 \text{ mg.g}^{-1}$  respectively for the adsorption of lead II and cadmium II onto sodic bentonite clay [9].

### 3.3. Effect of pH on sorption process

The effect of pH on the adsorption of lead(II) and cadmium(II) ions were studied at different pH values (2-10) using NK clay (amount of 0.1g) at constant metal ion concentration (60 ppm). The results indicate that the maximum adsorption of Pb(II) and Cd(II) ions takes place at pH 2.0 and 4.0. The adsorption capacity of the sorbent decreases with increase in pH of the medium (Figure 8).

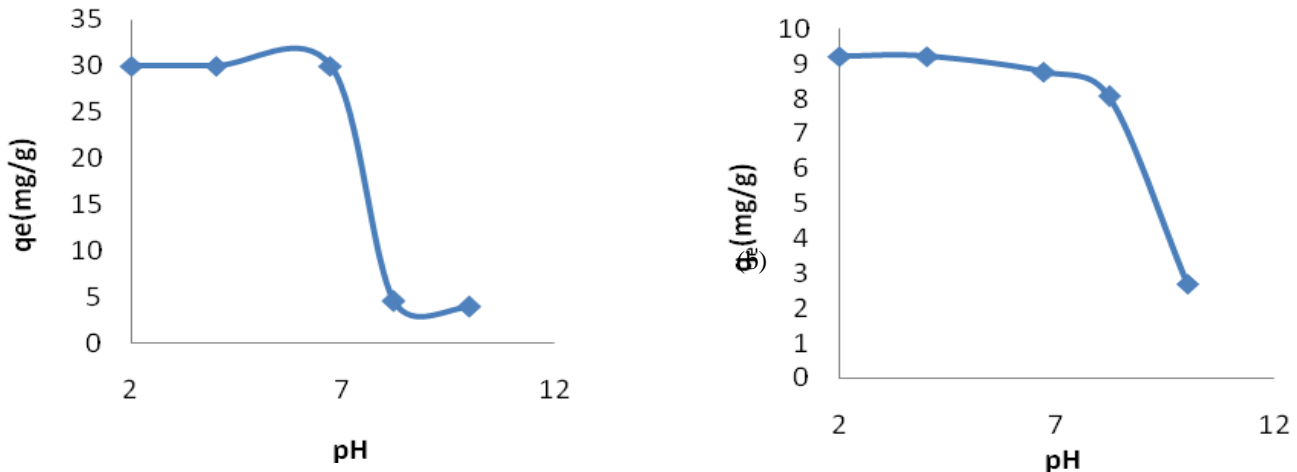


Figure 8: Effect of pH on adsorption of Cd(II) (a) and Pb(II) (b) on NK clay: room temperature, 0.1 g of clay in 50 mL of solution

Furthermore, in view of the results of characterization of NK clay including X-ray (figure 4), Fourier transform spectroscopy FTIR (figure 5), X-ray fluorescence (Table 1) and energy dispersive X-ray EDX (Figure 3), atoms such as the silicon (Si), magnesium II (Mg), calcium II (Ca), manganese II (Mn) and zinc II (Zn). These elements, lighter than the lead II and cadmium II and in the presence of hydroxyl ions  $\text{OH}^-$  (basic medium) could react very easily with these ions, thus leading to an exchange of ions between vacant sites left on the NK clay and Pb (II) and Cd (II) ions. But this is unlikely because of the fact that Pb (II) and Cd (II) ions will precipitate first by reaction with hydroxyl ions  $\text{OH}^-$  ions to form lead II hydroxide  $\text{Pb}(\text{OH})_2$  and cadmium II hydroxide  $\text{Cd}(\text{OH})_2$  precipitates which precipitates will also close the active sites of the clay material, that's the reason why the basification of the medium will tend to reduce the adsorption capacities of NK clay. However in acidic medium (atoms listed above may by action of acid release

their locations) this would lead to electrostatic attractions between positively charged cations such as Pb(II) and Cd(II) and negatively charged binding sites where large adsorption capacities observed in the acid pH. At pH values under the isoelectric point ( $\text{pH} < 6.7$ ), there is a net negative charge on the surface and the ionic point of ligands such as carboxyl, hydroxyl groups (see FTIR results at Figure 5) are free so as to promote interaction with the metal cations [10].

### 3.4. Effect of contact time and kinetics of metal sorption

Figure 9 represent the effect of the contact time on the retention of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  ions on NK clay at room temperature. The observation of these curves shows that the adsorption capacity increases with time and then stabilizes. This phenomenon is materialized by the bearing observed in the curve indicating the reduction of the numbers of vacant sites in the adsorbent. The amount of metal adsorbed versus time curves are smooth and continuous.

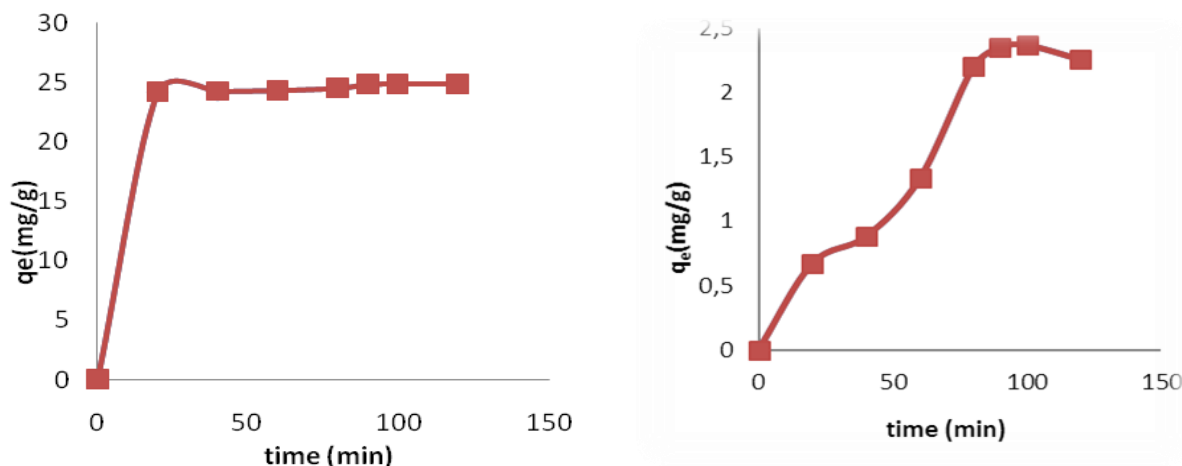


Figure 9: Effect of contact time on adsorption of Cd(II) (a) and Pb(II) (b) on NK clay: room temperature, 0.1 g of clay in 50 mL of solution

The kinetics of adsorption of pollutants are the same appearance characterized by a strong adsorption of  $Pb^{2+}$  and  $Cd^{2+}$  ions from the first minutes of contact, followed by a slow increase until it reaches an equilibrium state mostly 40 minutes for cadmium II and 90 minutes for lead II. The small variations at equilibrium are due to adsorption-desorption phenomena. The kinetics adsorption during the first minutes of reaction are too fast and can be interpreted by the fact that at the beginning of adsorption, the number of active sites on the surface of the adsorbent material is much more important than the sites left after a while.

These results show that the kinetics of fixation of  $Pb^{2+}$  and  $Cd^{2+}$  on clay is very fast. Equilibrium times 40 and 90 min of stirring respectively for cadmium and lead is maximum efficiency of the adsorption of  $Pb^{2+}$  and  $Cd^{2+}$  as well as the residual concentration of  $Pb^{2+}$  and  $Cd^{2+}$ . Beyond

the equilibrium time, the residual concentration of metal ions in solution varies by increasing or decreasing, this phenomenon is characteristic of a desorption or adsorption of pollutants. Several kinetic models were used in order to interpret experimental data [11, 12]. Control mechanisms of the process of adsorption, such as the chemical reaction, control of diffusion and mass transfer were reviewed.

These mathematical models were chosen for their simplicity and also for their applicability in the field of adsorption of the ions [13]. The models used are the pseudo-first order or Lagergren model and the pseudo-second order model.

The values of the first and pseudo-second order rate constants deduce from figures 10 and 11 are included in Table 3.

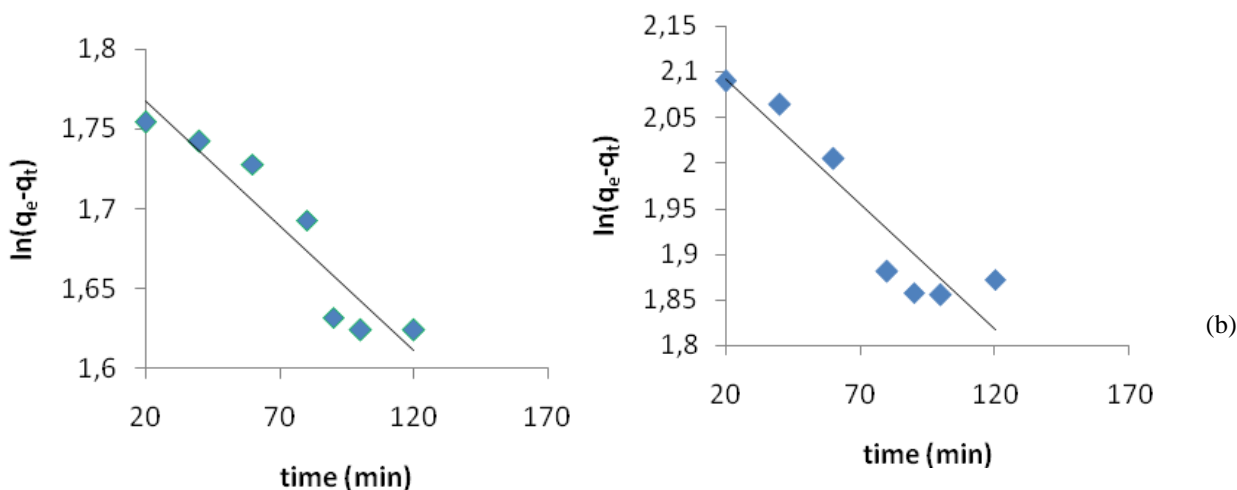


Figure 10 : First order or Lagergren kinetic model transforms curves of cadmium II (a) and lead II (b) on NK clay: room temperature, 0.1 g of clay in 50 mL of solution.

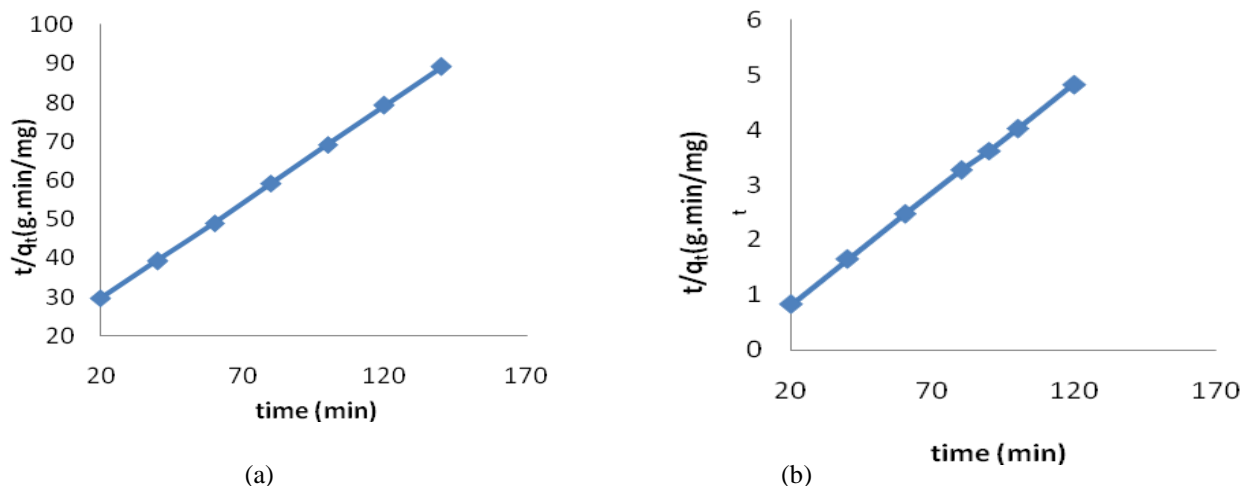


Figure 11: Pseudo-second order kinetic model transforms curves of cadmium II (a) and lead II (b) on NK clay: room temperature, 0.1 g of clay in 50 mL of solution.

Table 3: First order and second order constants for adsorption of Cd(II) and Pb(II) on NK clay

Metal ions	Pseudo-first order kinetic model			Pseudo-second order kinetic model		
	$k_1(\text{min}^{-1})$	$q_{\text{eth}}(\text{mg.g}^{-1})$	$R^2$	$k_2(\text{g.min}^{-1}.\text{mg}^{-1})$	$q_{\text{eth}}(\text{mg.g}^{-1})$	$R^2$
Pb(II)	0.0027	8.5557	0.8683	0.0126	2.011	0.9999
Cd(II)	0.0016	6.0436	0.8859	0.0302	25.126	0.9998

The correlation coefficients are low for the model of pseudo first order and border unit for the model of pseudo second order. So it's this second model that best describes the kinetics of adsorption of the two ions on NK clay. This kinetic has for main concern according to Ho and Mc Kay [14] to associate the adsorption process with the real reaction mechanism so the rate limiting step may be the chemical adsorption [15]. However pseudo-first order model adsorption constants are very weak and difficult to interpret which is not the case of the constants of the model of pseudo-second order confirming that this latest model best describes the adsorption of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  ions on the studied material. Similar results were obtained by Galindo et al. with the adsorption of these two metal ions onto sodic bentonite [9].

#### 4. CONCLUSION

In this study, Nkongsamba (Littoral Region of Cameroon) were used as a sorbent for the removal of cadmium(II) and lead(II) ions from aqueous solution. The sorbent is characterized on the basis of FTIR spectral study, XRD pattern study, X fluorescence study, EDX study and analysis of surface morphology. The Langmuir adsorption model and Freundlich equation are used for the mathematical description of the sorption of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  ions onto NK clays. The maximum adsorption capacities of the clay used in this study are  $56.50 \text{ mg.g}^{-1}$  for lead (II) and  $60.338 \text{ mg.g}^{-1}$  for Cadmium (II). Kinetics studies results suggest that the adsorption process follows second order kinetic model in both the cases. Equilibrium times are respectively 40 minutes for cadmium II and 90 minutes for lead II. In addition, better retention for low values of pH is observed. Batch studies show that it is possible to remove

the metal ions from aqueous medium through sorption onto NK clay.

#### REFERENCES

- [1] Fiche des données environnementales et toxicologiques de l'INRS, France, Décembre 2000.
- [2] A. Nsangou Y.,: « Évaluation du niveau actuel de contamination des poissons et des sédiments du lac municipal de Yaoundé en 2005 ».Mémoire de D.I.P.E.S.II, Chimie, ENS de Yaoundé, Université de Yaoundé I, Yaoundé, (2005)
- [3] S. Doyurum, A. Celik, Pb(II) and Cd(II) removal from aqueous solutions by olive cake, Journal of Hazardous Materials B138, 22–28, (2006)
- [4] Bina Sengupta, Mathurkumar S. Bhakhar and Ranjan Sengupta, Hydrometallurgy, Volume 89, Issues 3-4, December 2007, Pages 311-318.
- [5] F.Testard, L. Berthon and Thomas ; Comptes Rendus Chimie, Volume 10, Issues10-11, October-November 2007, Pages 1034-1041.
- [6] Anju Thekkedath, Wahib M. Naceur, Karima Kecili, Mohammed Sbai, Audrey Elana, Laurent Auret, Hervé Suty, Claire Machinal and Maxime ; Comptes Rendus Chimie, Volume 10, Issue 9, September 2007, Pages803-812.
- [7] Moustapha Belmoumen, Ali Assabbane and Yahia Ait Ichou ; Annales de Chimie Science des Matériaux, Volume 26, Issue 2, March-April 2001, Pages79-85.
- [8] Njoku, V.O., Oguzie, E.E., Obi, C., Bello, O.S. and Ayuk, A.A.; Adsorption of Copper(II) and Lead(II) from Aqueous Solutions onto a Nigerian Natural Clay; Aust. J. Basic & Appl. Sci., 5(5): 346-353, (2011)
- [9] Luz Stella Gaona Galindo; Ambrósio Florêncio de Almeida Neto; Meuris Gurgel Carlos da Silva; Melissa Gurgel Adeodato Vieira ; Removal of Cadmium(II) and Lead(II) ions from aqueous phase on sodic bentonite, Mat. Res. vol.16 no.2 São Carlos Mar./Apr. 2013 Epub Jan 28, 2013
- [10] Quek, S.Y., Ise, D.A.J., Forster, C.P., The use of sago waste for the sorption of lead and copper. Water SA. 24, 251–256, (1998).
- [11] SAMAKE D. Traitement des eaux usées de tannerie à l'aide de matériaux à base d'argile. Thèse, Université Joseph Fourier de Grenoble, pp. 31-47, (2009)



- [12] Al-Sultani K.F. and Al-Seroury, Characterization the removal of phenol from aqueous solution in fluidized column by rice husk adsorbent, *Res.J.Recent.Sci.*,1, PP145-151, (2012)
- [13] BOH-LERE SIRYABE, Caractérisation géotechnique, physico-chimique et minéralogique des argiles de Nkongsamba et Missolet II, (2012).
- [14] Y. S. HO and G. McKay, A comparison of chemisorption kinetic models to pollutant removal on various sorbents, *Trans IChemE*, Vol 76, Part B, November 1998.
- [15] Chiou, M.S., Li, H.Y., Equilibrium and kinetic modeling of adsorption of reactive dye on cross-linked chitosan beads enhanced abilities of highly swollen chitosan beads for colour removal and tyrosinase immobilization. *J. Hazard. Mater.* 93 (2), 233–248, (2002).