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Adsorption of Pb^{2+} Ions on two clays: Smectite and kaolin the role of their textural and some physicochemical properties

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Abstract

The present work examined the influence of textural and some physico-chemical properties of two clays smectite and kaolin in the removing of lead (II) ions in aqueous solutions. The influence of some environmental parameters such as pH, contact time and initial concentration were examined. Residual lead concentration reaches equilibrium in 30 minutes for Smectite and 40 minutes for kaolin. The pseudo-second order and Elovich kinetics models best described adsorption kinetics on kaolin whereas the pseudo-first order or Lagergren kinetic model followed the lead (II) sorption on Smectite. For the two clays intraparticle diffusion seems to be the rate limiting-step. Batch sorption studies showed that Langmuir model gives a better fit for the two clays compared to the Freundlich adsorption isotherm. Adsorption mechanism is due essentially to the electrochemical ion-exchange between lead (II) and clays surfaces and the complexation reaction. Mineralogical composition of each clay strongly influences the sorption process.

Keywords: smectite, kaolin, isotherm, kinetics models, ion-exchange.

1. Introduction

The release of heavy metals in the environment is a major problem throughout the world. This problem, because it causes pollution in the waters, groundwater, soil, air and even in food concerns everyone [1]. In Cameroon, several heavy metals are generally found in drinking water, wastewater, rivers and lakes mainly mercury (Hg), lead (Pb), cobalt (Co), nickel (Ni), copper (Cu) and zinc (Zn) in varied proportions (50-1000 ppm). In the city of Yaoundé (Cameroon's capital), the work conducted by Demanou and Brummett [2] in two lakes in the city (Central Lake and Lake Melen) showed the presence of several metals among which lead (II) which is by far the most toxic where the interest in this metal in this work. It is therefore necessary to minimize the amount of lead (II) which may thus be found in critical concentrations in consumption waters, air and even by bioaccumulation in the food chain. Lead penetrates in the human body at the time of ingestion of food (65% of the cases), of water (20% of the cases) and by the air (15% of the cases) [3]. It harms very seriously health and the environment. It causes several undesirable effects on the living beings inter alia: the disturbance of the biosynthesis of haemoglobin, anemia, increase in the blood pressure [4], the miscarriages, renal problems, damage of the brain, decline of the fertility of the men, the disturbance of the behavior of the children (aggressiveness, impulsive behavior, hyperactivity) [3]. In the environment the watery organizations and ground suffer enormously from poisoning to lead. The motorways and the arable lands undergo this pollution because lead disturbs the functions of the ground.

The standards (acceptable lead rates in drinking water) evolved much during the years. In 1984 the acceptable concentration was of 50 $\mu\text{g/L}$ in France and in Canada [3]. In 1990 it decreased and passed to 10 $\mu\text{g/L}$ for Canada and 25 $\mu\text{g/L}$ for France. The value of 10 $\mu\text{g/L}$ is besides that recommended by the World Health Organization (WHO).

Physical and chemical processes have been extensively studied to remove lead (II) from aqueous solutions like adsorption, direct precipitation, reverse osmosis, ultrafiltration, electrochemical methods, evaporation and ions exchange [5, 6]. But adsorption can be seen as an efficient and economic method for removal of lead at low concentration as in Cameroon's waters.

That's why considerable attention is devoted in this work to remove lead (II) ions in aqueous solution by adsorption on two clays: smectite and kaolin.

Activated carbon has been the most popular adsorbent due to its high surface area, high adsorption capacity, and high degree of surface reactivity [7, 8] but the application of activated carbon for wastewater treatment is not feasible due to its high price and cost associated with the regeneration because of high-degree of losses in real process [9]. Indeed, clays appear to be an economically attractive alternative in the adsorption of heavy metals such as lead (II) even more as the clay deposits are abundant in Cameroon. Authors such as Abd-Elfaitahand Kojiwa [10], Yadava *et al.* [11], Orumwense *et al.* [12], Barbier *et al.* [13], Hizal and Apak [14], Adebowale *et al.* [15], Unuabonah *et al.* [16], Sari *et al.* [17] and Olgun and Atar [9] have carried out studies on the adsorption of lead (II) with clays of different origin and highlighted the ability of these to adsorb Pb^{2+} ions in aqueous solution.

The present work investigates the potential use of two clays (smectite and kaolin) as a metal sorbents for the removal of lead (II) ions from aqueous solutions. Environmental parameters affecting the adsorption process such as pH, contact time, initial metal ion concentration were studied. The role of textural and some physico-chemical properties of the two clays in the adsorption process were also studied. The equilibrium adsorption data were evaluated by using Freundlich and Langmuir isotherm models. The kinetics studies using four kinetics models (Pseudo-first order or Lagergren model, Pseudo second order, Elovich and Weber and Morris intraparticle diffusion) were carried out.

2. Materials and Methods

2.1. Adsorbents and characterization

Two clays smectite and kaolin which the origin and the aspect are presented in Table-1 were used in this study.

Table 1: Origins and aspects of smectite and kaolin used

Clay material	Origin	Physcia aspect	
		Color	Consistency
Smectite	Sabga- North west region-Cameroon	White	Powdery and not very compact
kaolin	France	White	Compact but brisable with hand

Smectite and kaolin were dried at 110 °C for 24 hours. After being dried they were ground and sieved. The main crystalline compounds in samples were identified by qualitative X-ray powder diffractometry (XRD) using a Siemens D5000 X-ray powder diffractometer with the characteristic Cu radiation and a scintillation detector. For the two clays samples, XRD analysis was carried out several times. The identification of compounds was performed through comparison with standards in the Joint Committee of Powder Diffraction Standards (JCPD) issue 2010.

Scanning electron micrographs (SEM) of the two clays were recorded by a FEI Quanta 200 FEG (Field Emission Gun) ESEM operated at 15-20 kV. Since this material collected charges on its surface, the low vacuum mode was used instead of high vacuum mode generally used.

The BET surface areas and porosity of smectite and kaolin were calculated from N_2 adsorption by using the Brunauer–Emmett–Teller (BET) method with Micrometrics model Asap 2020 instrument.

2.2. Adsorption and kinetics studies

The various lead solutions are obtained starting from lead nitrate $Pb(NO_3)_2$. A lead nitrate was obtained from Sigma-Aldich Corporation (St Louis, MO). Solutions of lead of concentrations ranging between 60 and 150 ppm were prepared.

In each of 6 Flask's (for each material) of 100 mL, 0.05 g of clay was placed and 50 mL of aqueous solution of Pb^{2+} added. The solution concentrations were respectively 60, 70, 90, 110, 130, 150 ppm. All the mixtures thus obtained are agitated 15 at the same time on a magnetic stirrer of type Variomag (Electronic rührer Multipoint HP15) at a temperature of 25 °C and a speed of 500 rpm during one

night to reach equilibrium. At equilibrium each sample is filtered and the residual concentration is determined by ICP/OES.

The device is same as that previously described but the kinetic study is made only on the concentration of 60 ppm and in this case the aliquots were drawn every five minutes into a pipette Pasteur and filtered in order to remove any clay particles and their concentrations measured by ICP/OES. It is realized that at the end of 30 minutes for smectite and 40 minutes for kaolin the concentration does not change any more, thus the equilibrium adsorbed concentration is reached.

After adsorption on the various studied adsorbents, the different filtrates were diluted by a nitric acid solution HNO_3 1M. The analysis of the lead samples was carried out by using a ThermoCAP 6500 inductively coupled plasma-Optical Spectrometry Emission (ICP/OES).

2.3. pH measurements

0.05 g of each clay sample was mixed in 50 mL of distilled water under a temperature of 25 °C to determine the pH of the solution containing the clay before and after adsorption of lead (II). After agitation, the pH of each sample was measured with a pH-meter of the type METTLER TOLEDO MP220.

3. Results and Discussion

3.1. XRD spectra of the smectite and kaolin

XRD spectra of the two samples are represented below (spectra XRD are represented and their examination also) (Fig 1 and Fig 2 for smectite and kaolin respectively).

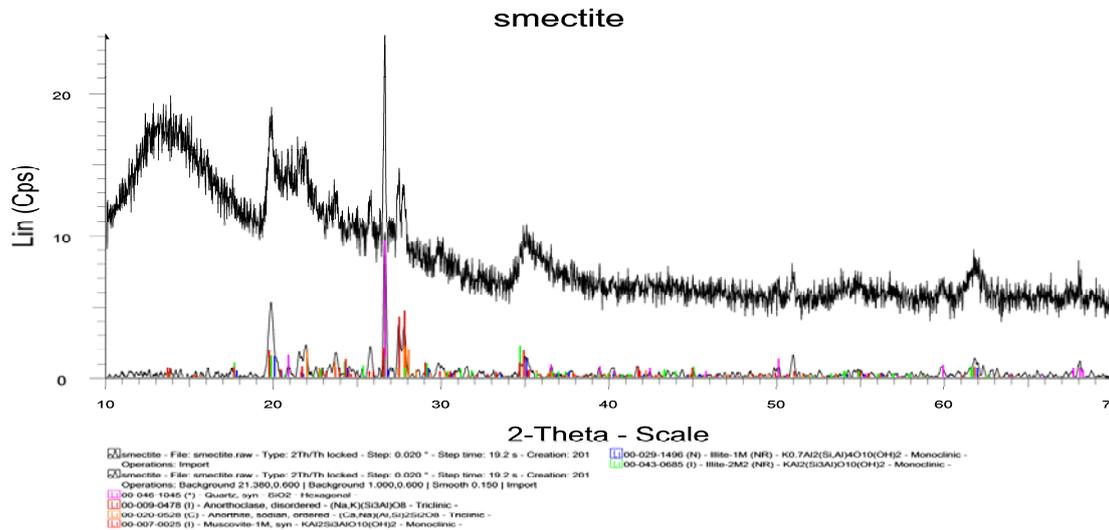


Fig 1: XRD pattern of smectite.

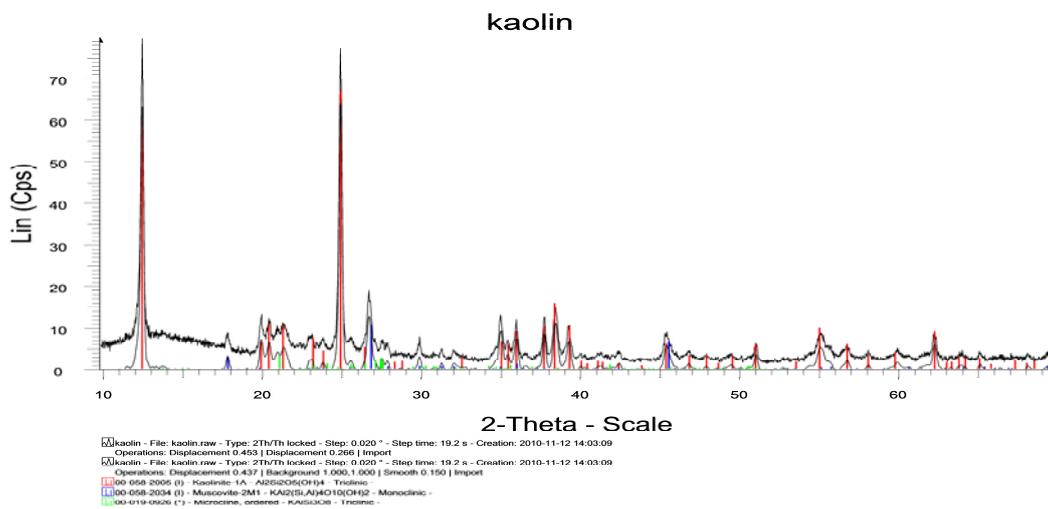


Fig 2: XRD pattern of kaolin

The XRD pattern of smectite shows that it is a very small crystal that's mainly X-ray amorphous. Some minerals could be identified with more or less certainty (see Fig. 1): Quartz SiO_2 , Anorthoclase $(\text{Na,K})(\text{Si}_3\text{Al})\text{O}_8$, Anorthite $(\text{Ca,Na})(\text{Al,Si})_2\text{Si}_2\text{O}_8$, Muscovite $\text{KAlSi}_3\text{AlO}_{10}(\text{OH})_2$ and illite $\text{KAl}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2$. XRD pattern of kaolin (Fig. 2) presents a completely crystalline material. The minerals such as kaolinite $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_5$, muscovite $\text{KAl}_2(\text{Si,Al})_4\text{O}_{10}(\text{OH})_2$, and microcline KAlSi_3O_8 were found. The minerals observed on these clays will play a very important part in the adsorbent properties of these materials.

3.2. SEM micrographs and observations

SEM micrographs of smectite and kaolin are represented in Fig. 3 and 4. SEM micrographs of the two studied clays present homogeneous surfaces in the form of plates. The two clays are made of variable cluster of different sizes with a prevalence of the particles in spherules. Some porosity is observed on the surface of these two clays what predict interesting adsorbent properties.

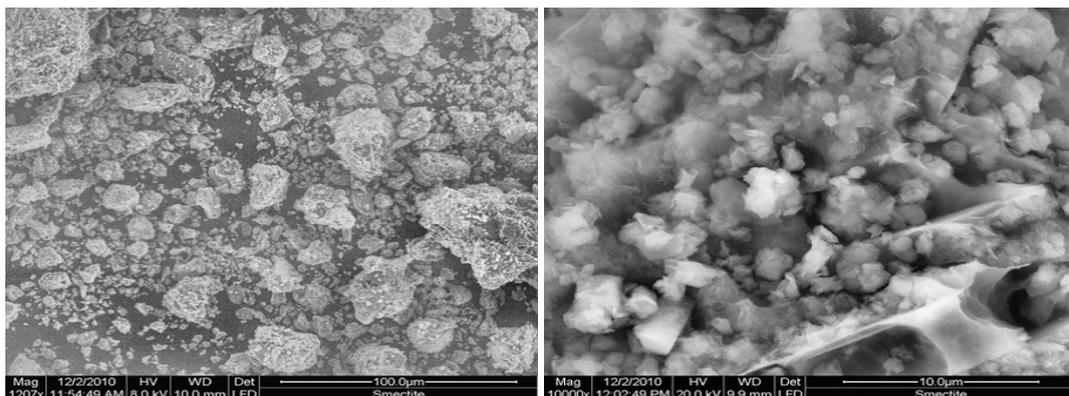


Fig 3: SEM micrographs of smectite at 100 µm and 10 µm
~ 795 ~

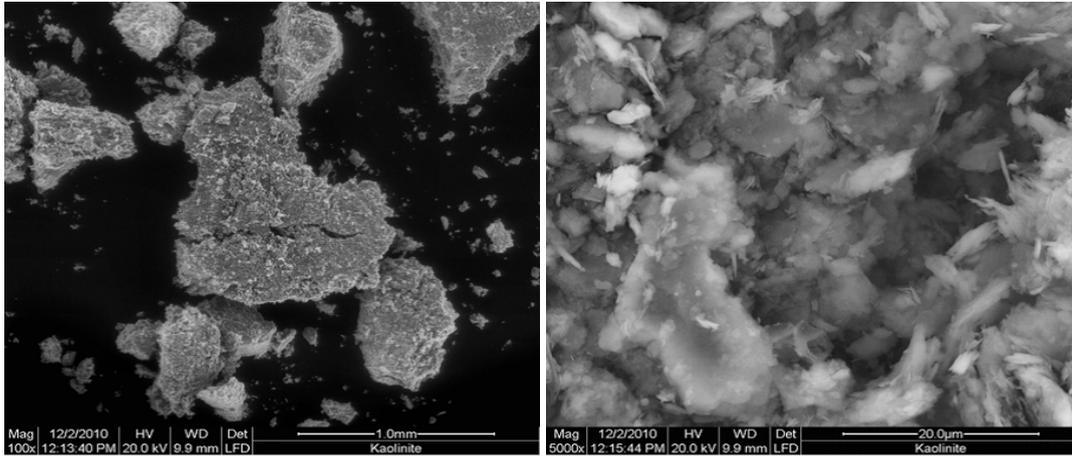


Fig 4: SEM micrographs of kaolin at 1 mm and 20 µm

3.3. Specific surfaces and porosity

The adsorption-desorption isotherm of nitrogen N₂ onto smectite and kaolin samples are represented respectively by Figs 5 and 6.

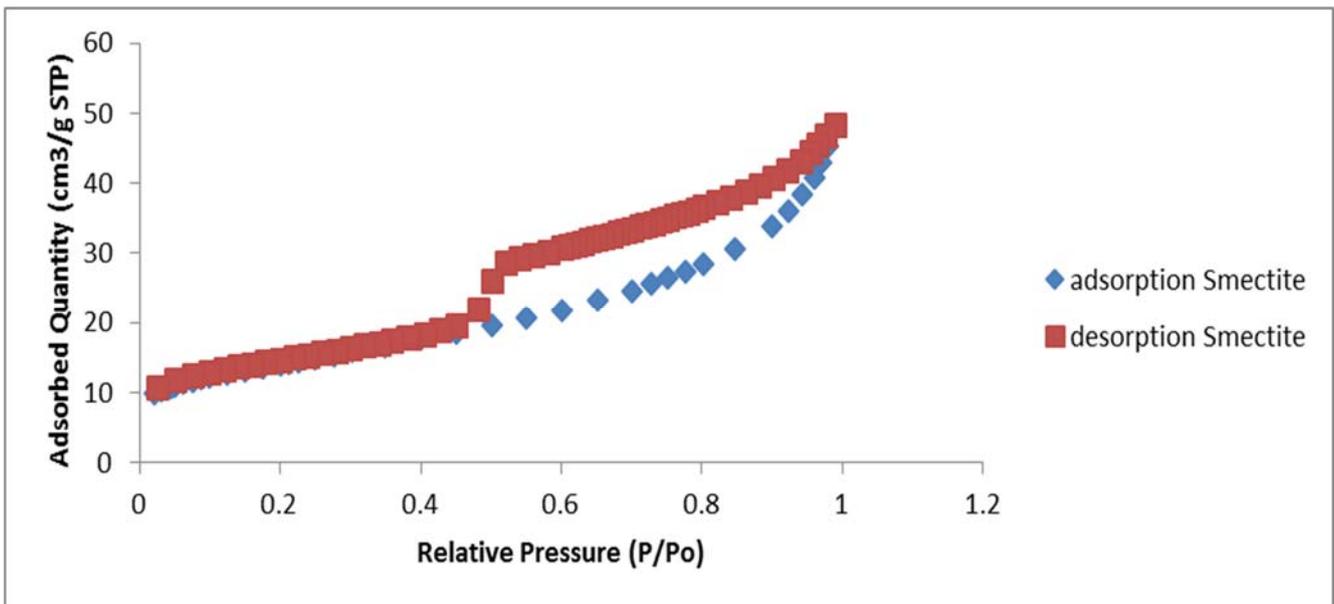


Fig 5: Adsorption-desorption isotherms of N₂ onto Smectite

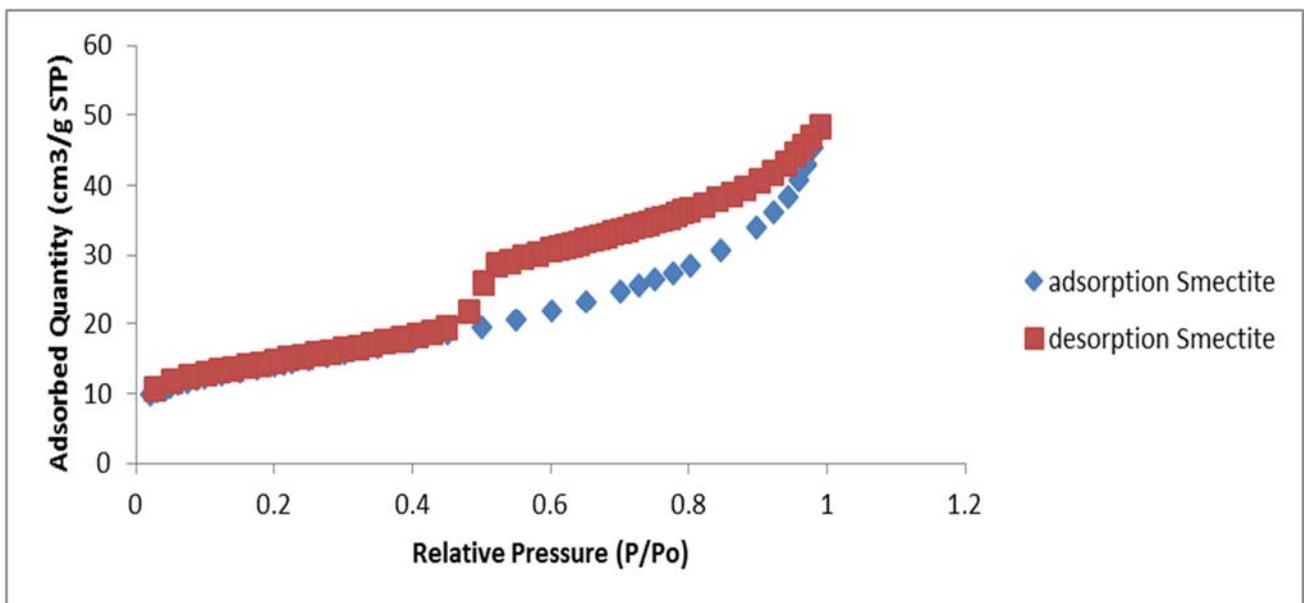


Fig 6: Adsorption-desorption isotherms of N₂ onto kaolin

The isotherms of smectite (Fig. 5) are of type IV characteristic of a multi-layer adsorption with a medium slightly porous. This observation is confirmed by the SEM micrograph on Fig. 3. These isotherms have a hysteresis resulting from a capillary condensation. The form of this hysteresis indicates the presence of the pores in bottles with a neck a little lower than the body [18]. These broad loops of hysteresis are due to the presence of cracks or of slits in which the molecules of nitrogen do not desorb in the same way anymore of which they were adsorbed from where multi-layer adsorption. The isotherms of adsorption-

desorption of the kaolin (Fig. 6) is of type II characteristic also of a microporous medium [18] but here one does not observe a hysteresis.

The specific surfaces area determined by BET (linear transformer on Fig. 7), BJH adsorption and desorption, the total volume of pores obtained by adsorption at a given (definite relative pressure) and for a given pore size are presented in Table-2. The size of the pores obtained by BET using the relation $4V/A$ and sizes of nano particles of smectite and kaolin are also shown in Table-2.

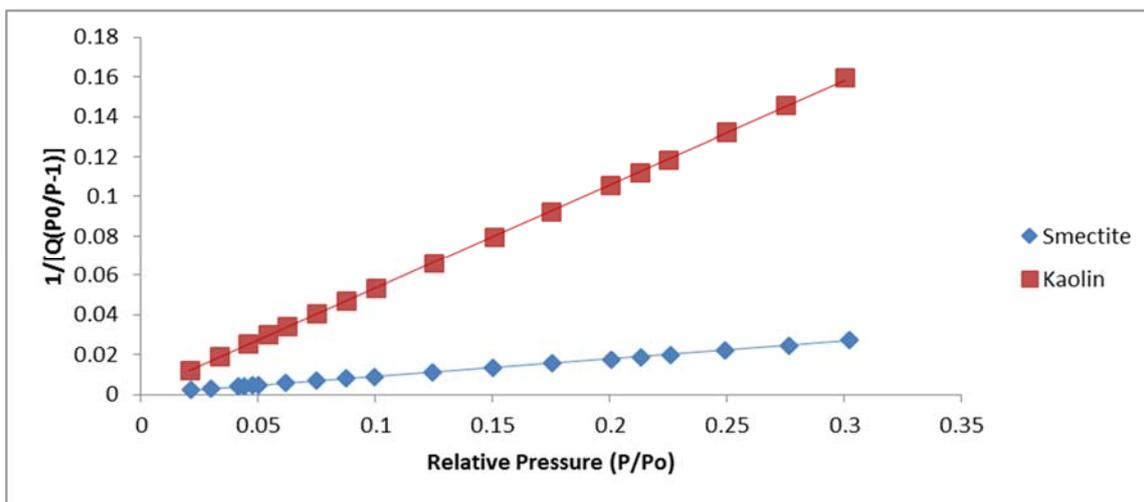


Fig 7: BET isotherm linear transformer of smectite and kaolin

Table 2: Specific surface area and porous volume of smectite and kaolin

Adsorbent	Surface area (m ² /g)			
	Single point area	^a BET surface area	^b BJH Adsorption cumulative surface area of pores between 17 Å and 3000 Å	BJH Desorption cumulative surface area of pores between 17 Å and 3000 Å
Smectite	P/P ₀ =0.302016244 48.1489	49.2297	49.326	56.2773
Kaolin	P/P ₀ =0.300071712 8,1703	8.2902	8.437	8.8058
Adsorbent	Pores volume (cm ³ /g)			
	Single point adsorption total pore volume of pores	BJH Adsorption cumulative volume of pores between 17 Å and 3000 Å width	BJH Desorption cumulative volume of pores between 17 Å and 3000 Å width	
Smectite	less than 1954.523 Å width at P/P ₀ =0.990010 0.07474	0.076763	0.075463	
Kaolin	less than 2519.657 Å width at P/P ₀ =0.992277 0.025803	0.026022	0.023650	

^aBET specific surface area: Brunau-Emmett-Teller surface area obtained using BET linear transformer equation from the data of Fig. 7; ^bBJH: Barrett-Joyner-Halenda surface area given by the Micromeritics model Asap 2020 instrument

Specific surfaces of the two samples of clay smectite and kaolin are respectively about 49.23 and 8.26 m²/g and porous volumes of about 0.074 and 0.026 cm³/g respectively.

3.4. Sorption equilibrium

The effect of initial concentration on the percentage removal of Pb (II) is shown in Fig. 8. It is apparent from the figure that the percentage removal decreases with the increase in the Pb (II) concentration. For Pb (II) at same adsorbent dose (0.05g) and contact time (equilibrium time equal to 40 minutes for kaolin and 30 minutes for smectite), a slight drop in percentage removal at higher concentration was observed. At low concentrations, sufficient adsorption sites are available for adsorption of the Pb (II) metal ions. Therefore,

the fractional adsorption was observed to be independent of initial metal ion concentration. However, at higher concentrations the numbers of heavy metal ions are relatively higher compared to the availability of adsorption sites. Hence the percentage removal of Pb (II) on the initial metal ions concentration decreases with increase in initial Pb²⁺ ions concentration. Olgun and Atar [9], showed during the studies of adsorption of lead (II) onto clay mixture containing boron impurity that at lower concentration, all metal ions present in the solution contact with the binding sites of a clay, thus, the adsorption is independent of the initial metal ions concentration but higher concentration, the lower adsorption yield is due to saturation of the adsorption sites.

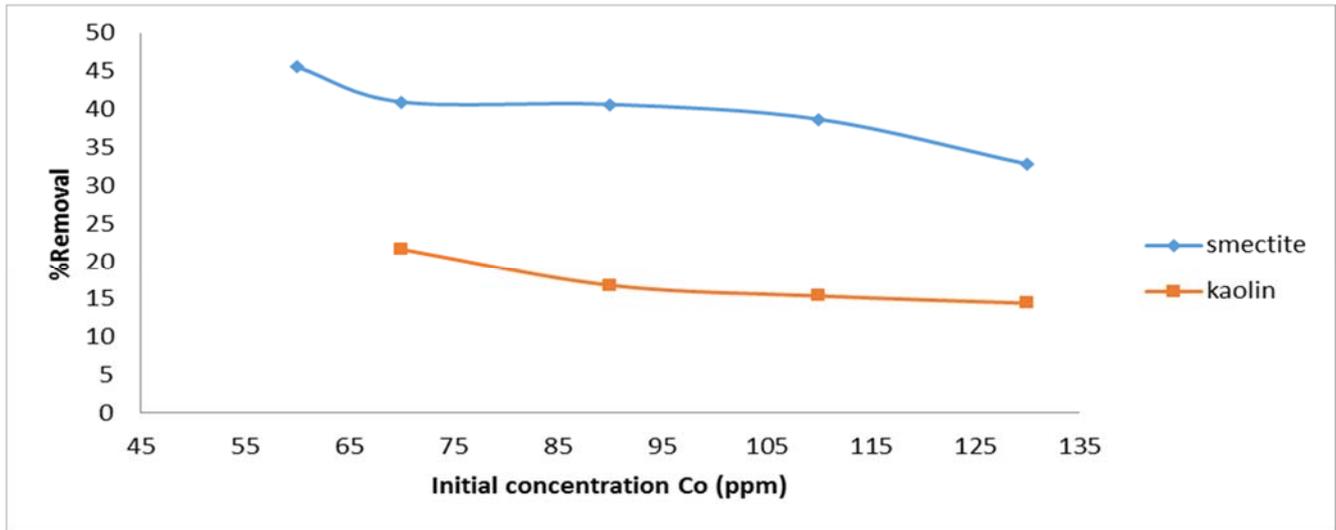


Fig 8: Effect of initial concentration on the adsorption of lead (II) onto smectite and kaolin

pH is one of the most important parameters controlling the uptake of heavy metals from wastewater and aqueous solutions. The pH of the various solutions containing materials studied before adsorption and after adsorption of the Pb²⁺ ions are showed in Table-3. In general way, the pH does not vary much when the concentration of metal ions increases for the same sample because the concentrations

studied are very close. But in smectite pH decreased when concentration of Pb (II) ions increased. This result is the same as that obtained by Martinez and Motto ^[19] showing that pH in the aqueous phase decreases when the concentration increases. In kaolin, pH does not vary much when concentration increased. The mineral composition of the two clays may explain these differences.

Table 3: pH of lead solutions containing smectite and kaolin

Adsorbent Concentrations (ppm)	smectite					kaolin				
	0	70	90	110	130	0	70	90	110	130
pH	6,97	5,51	5,16	4,97	4,9	4,72	5,6	5,78	5,62	5,09

Orumwense *et al.* ^[12] showed during the adsorption of lead (II) on kaolinitic clay from Giru-Nigeria that acidic pH as in this work favored adsorption of Pb²⁺ ions. But Adebowale *et al.* ^[15], Barbier *et al.* ^[13] and Olgun and Atar ^[9] obtained different results by showing that increasing pH of solutions of metal ions increased the removal percentage of Pb²⁺ ions on clays. The experimental conditions could explain this result. Indeed, in the work of Adebowale *et al.* ^[15], the adsorption of Pb (II) ions on kaolinitic clay was performed in the presence of Cd (II) ions which could have created a competition so increasing pH may increase the mobility of Pb²⁺ ions. It is the same for adsorption of Pb²⁺ ions onto clay mixture containing boron impurity done by Olgun and Atar

^[9] in the presence of Ni²⁺ ions. Moreover Barbier *et al.* ^[13] adsorbed lead (II) ions onto phosphate-modified kaolinitic clay.

In order to determine the adsorption parameters of lead II on studied activated carbons, Freundlich and Langmuir isotherms have been studied. The various constants characteristic of adsorption for each model and each sample were obtained by using MS Excel of Windows. All the constants are found in Table-4. The different parameters of these equilibrium models often provide some insight into both the sorption mechanism and the surface properties and affinity of sorbent ^[20].

Table 4: Adsorption constants of Pb (II) adsorption smectite and kaolin

Adsorbent	b _F	^c Freundlich			^d Langmuir			
		n	a _F ((mg/g). (mg/L) ^{-1/n})	R ²	K _L (L/g)	A _L (L/mg)	Q _L (mg/g)	R ²
Smectite	0,5117	1,9542	4,2516	0,889	1,0819	0,01396	77,519	0,948
Kaolin	0,5276	1,8954	1,6253	0,7875	0,4527	0,0189	30,395	0,788

^bb_F(Reverse of the constant of no acidity), n(constant of no acidity), a_F(Freundlich partition's constant) were obtained from the linear form of the Freundlich isotherm equation using data from Fig. 8; ^dK_L(Langmuir intensity constant), A_L(Langmuir constant), Q_L(Adsorption capacity) were obtained from the linear form of the Langmuir isotherm equation using data from Fig 8; ^{c,d} R²(correlation coefficients) obtained from the linear relationship of Freundlich and Langmuir isotherms

The two isotherms have very low determination coefficient R² which explain the difficulty of these two isotherms to explain the adsorption of the Pb²⁺ ions onto the two clay samples. But with a value of K_L= 1.0819L/g, smectite seems to have a rather important affinity with respect to the Pb²⁺ ions than kaolin (K_L=0.4527L/g) that's the adsorption is seen to be highest in smectite. The values of n the heterogeneity

factor lie between 1 and 10 indicating favorable adsorption of Pb²⁺ ions onto the two clays. Adsorption capacity as indicated by value of Q_L is seen to be maximum for smectite (77.52mg/g) and lower for kaolin (30.395 mg/g) what's in agreement with the values of K_L above.

The Langmuir model gives a better fit for the two clays compared to the Freundlich adsorption isotherm.

Adebowale *et al.* [15] showed a satisfactory fit with Freundlich isotherm during lead (II) adsorption onto unmodified kaolinitic clay but a low concentration data also showed satisfactory fits to Langmuir isotherm. Olgun and Atar [9] showed that on the adsorption of lead (II) onto clay mixture with boron impurity, the Langmuir model gives a better fit compared to the Freundlich adsorption isotherm as in this work.

Taking into account the low content of Pb^{2+} ions in the Cameroonian waters, a particular accent is carried to concentration 60 ppm (which was retained to make the kinetic studies in the continuation) for which the percentages of adsorption and the k_d -values are presented in Table-5.

The K_d -value is a factor related to the concentration of a contaminant (in this study lead) between the solid (smectite or kaolin) and the aqueous solution. It's the ratio of the quantity of the sorbate adsorbed per mass of adsorbent to the amount of sorbate remaining in solution (see equation below).

The adsorption percentage is the relationship between the quantity of adsorbed species and the initial quantity.

Table 5: K_d -values measurements and adsorption percentage of lead (II) onto kaolin and smectite at 60 ppm

Adsorbent	smectite	kaolin
Initial concentration (ppm)	60 ppm	
%Adsorption	46.63	21.45
eK_d -values (cm^3/mg)	757.0481	270.4333

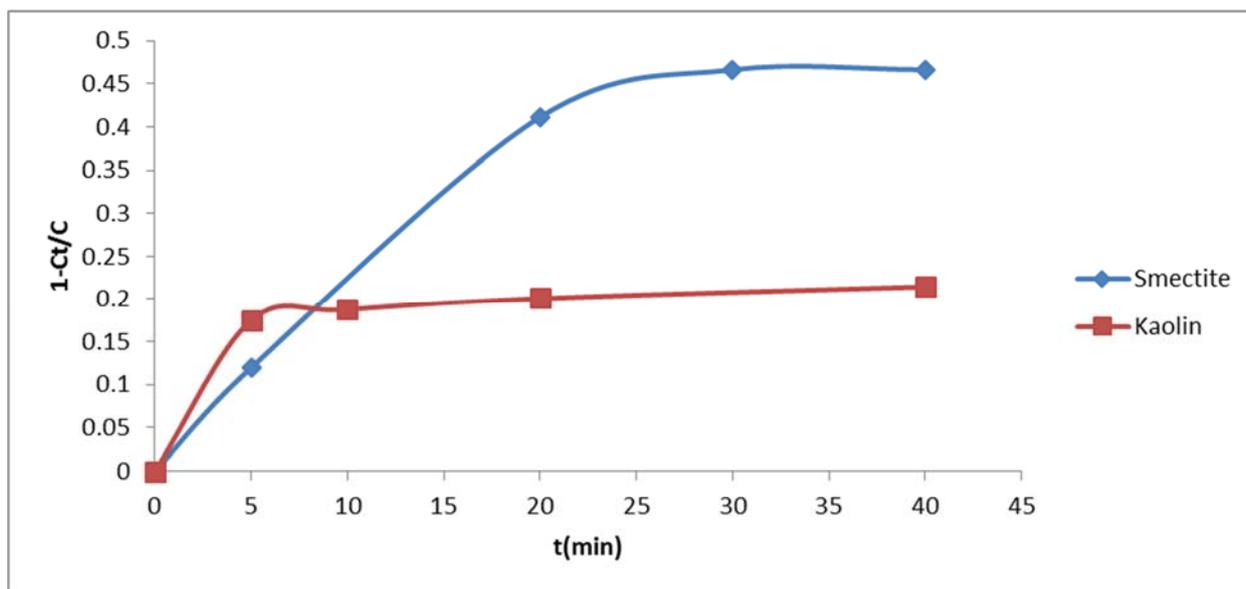


Fig 9: Time variation of Pb (II) adsorption on smectite and kaolin (Conditions: $C_0=60$ ppm, rate=500rpm and $T=25$ °C)

Contact time required for the maximum removal of lead (II) by smectite and kaolin (Fig. 9). There is step increase in the adsorption in the initial stages of the reaction as seen in the curves. The time variation curve is smooth and continuous for the two clays and this indicates the formation of monolayer coverage on the outer interface of the adsorbent. These results reveal that the uptake of sorbate species is fast at the initial stage of the contact period and thereafter it becomes slower near equilibrium (Fig. 8). Between these two stages of the uptake, the rate of sorption is found to be nearly constant. This is obvious by the fact that a large number of vacant sites are available for sorption during the initial stage, and after a lapse of time the remaining vacant surface sites

eK_d -value: values obtained using the above equation

Smectite with an adsorption percentage of 46.63% adsorbs much more Pb^{2+} ions than kaolin (21.45%). This result is in agreement with that observed in batch sorption studies of Freundlich and Langmuir isotherms previously made. This is well explained by the physicochemical properties. Specific surface areas (and porous volume) are respectively 49.23 m^2/g and 8.29 m^2/g (and 0.075 cm^3/g and 0.026 cm^3/g) for smectite and kaolin. These properties explained why lead (II) is more adsorbed on smectite than on kaolin. Moreover SEM micrograph observation (Figs 3 and 4) showed that smectite surface's seems more porous than kaolin one.

In addition, the k_d -values measured (757.05 cm^3/mg for smectite and 270.43 cm^3/g for kaolin) show that lead (II) is readily sorbed on the surfaces of the two clays studied but more onto smectite.

3.5. Kinetics studies

The rate of metal sorption is an important factor and a prerequisite for determining the reactor design and process optimization for a successful practical application [9]. To establish an appropriate contact time effect between the two clays and the Pb(II) ions solution, sorption capacities of metal ions are measured as a function of time at 60 ppm (see Fig. 9). The removal of lead (II) was shown to increase with time and attained a maximum value at 30 minutes for smectite and 40 minutes for kaolin. After these equilibrium times the amount removed remain constant.

are difficult to be occupied due to repulsive forces between the solute ions on the solid and the bulk phase. Several authors who have studied the adsorption of Pb^{2+} ions on clays have reached equilibrium at similar time and made the same observations as in this work. Thus Olgun and Atar [9] during the adsorption of lead(II) onto clay mixture containing boron impurity reached equilibrium after 45 minutes. A relatively short time 20 minutes was found by Adebowale *et al.* [15] with kaolinitic clay and a relatively long time of 90 minutes was found by Yadava *et al.* [11] on China clay.

The rates of the adsorption have been tested with the Lagergren or pseudo-first order, pseudo-second order, Elovich and Weber and Morris intraparticle diffusion

kinetics models. The adsorption results as function of time are studied by the four kinetic models and the obtained

statistics parameters based on linear regression (Figs 10-13) for all the four models are given in Table-6.

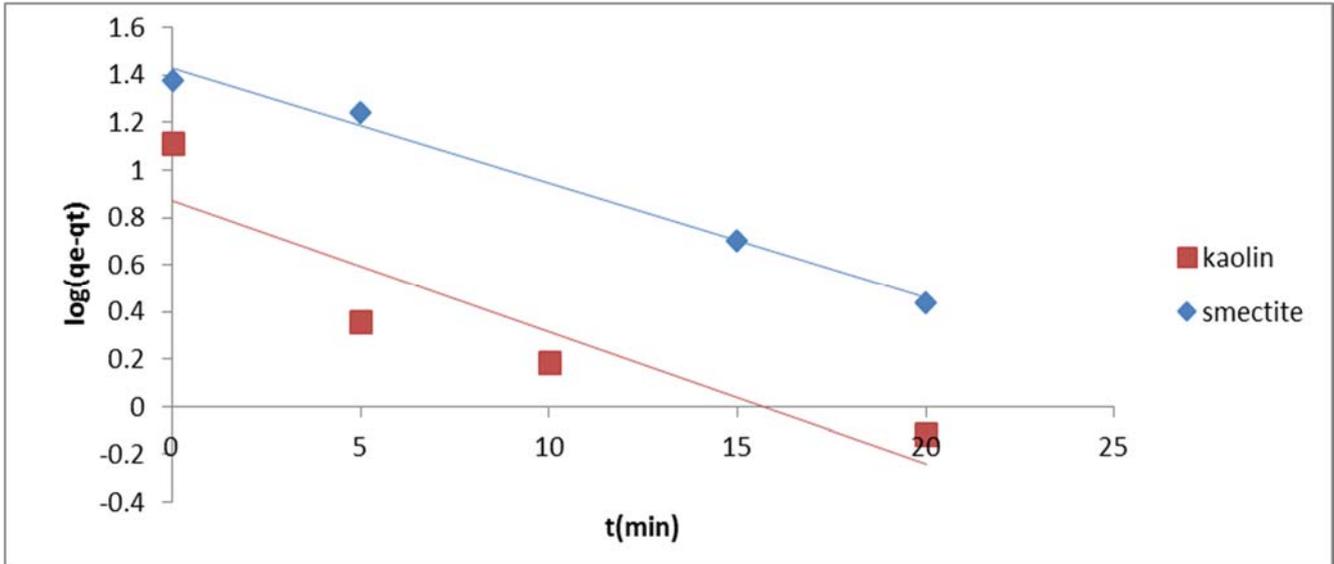


Fig 10: Lagergren plots of the removal of Pb²⁺ ions by adsorption onto smectite and kaolin

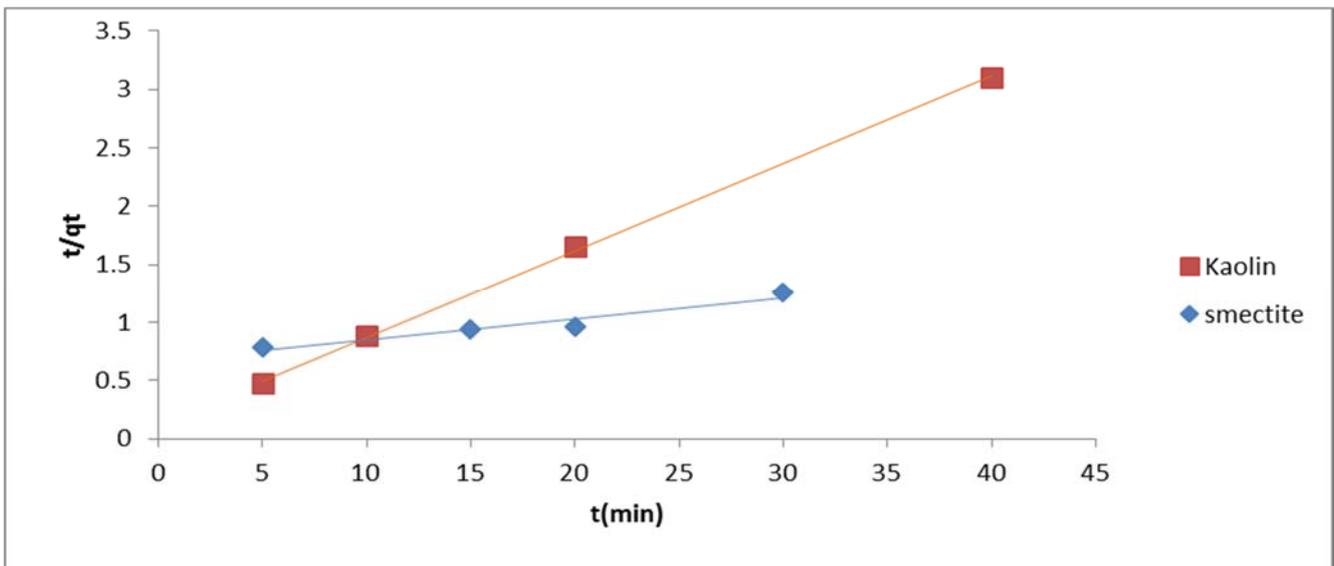


Fig 11: Pseudo-second order plots of the removal of Pb²⁺ ions by adsorption onto smectite and kaolin

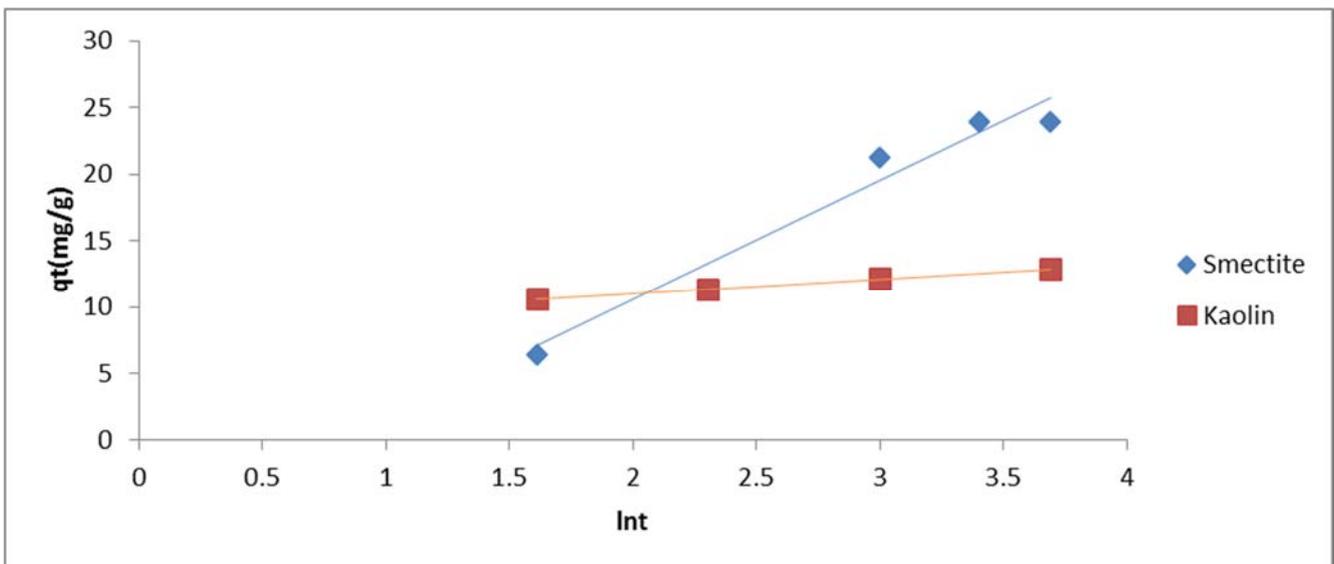


Fig 12: Elovich plots of the removal of Pb²⁺ ions by adsorption onto smectite and kaolin

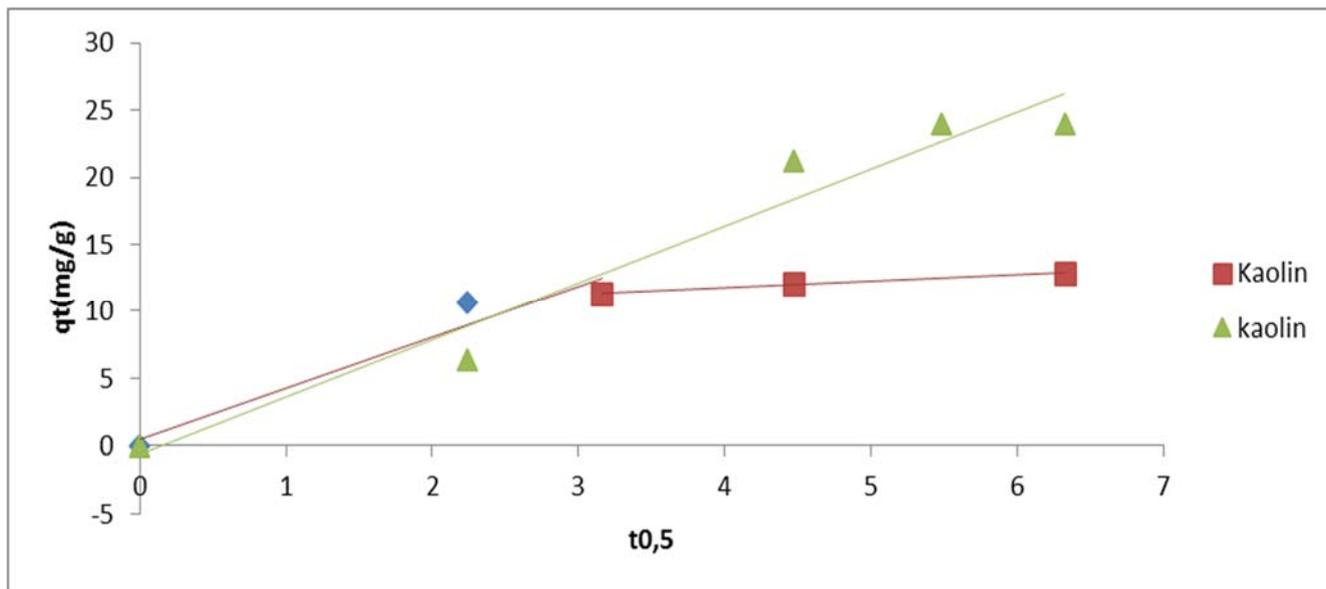


Fig 13: Weber and Morris intra-particle diffusion plots from the removal of Pb²⁺ ions by adsorption on smectite and kaolin

Table 6: Adsorption kinetic model rate constants for smectite and kaolin

Adsorbent	Kinetic Models								
	^f Pseudo-first order				^g Pseudo-second order				
	q _{e,exp} (mg/g)	q _{e,calc} (mg/g)	K ₁ (min ⁻¹)	R ²	q _{e,exp} (mg/g)	q _{e,calc} (mg/g)	K ₂ (g/mg.min)	h(mg/g.min)	R ²
Smectite	23,9377	26,6563	0,1119	0,989	23,9377	55,2486	0,00049	1,5008	0,927
Kaolin	12,8873	7,4012	0,1274	0,823	12,8873	13,3511	0,04583	8,1699	0,999
Adsorbent	Kinetic Models								
	^h Elovich model			ⁱ Weber and Morris intra-particle diffusion					
	α(mg/g.min)	β(g/mg)	R ²	K _{id1} (mg.g ⁻¹ .min ^{-0,5})	K _{id2} (mg.g ⁻¹ .min ^{-0,5})	C ₁	C ₂	R ²	
Smectite	3,9321	0,1111	0,966	/	4,2406	/	-0,6119	0,957	
Kaolin	3451,43	0,9116	0,999	3,8029	0,5479	0,4768	9,523	0,948/0,979	

^fq_{e,exp} and q_{e,calc} are respectively experimental and calculated amount of lead adsorbed at equilibrium, values of q_{e,calc} are obtained from the linear form of the Lagergren and pseudo-second order equation using data from fig. 10 and 11; ^gK₁ and K₂ are respectively pseudo-first and pseudo second order constant obtained from the linear form of the Lagergren and pseudo-second order equation using data from fig. 10 and 11; ^hα and β are respectively Elovich speed constant and Elovich desorption constant obtained using linear form of the Elovich equation using data from fig. 13; ⁱK_{id1} and k_{id2} are intraparticle diffusion constants obtained from the Weber and Morris equation by using data from figures

The kinetic of pseudo-second order and Elovich models with correlation coefficients both close to 1 seem to be those which explain best the adsorption of the Pb²⁺ ions in the kaolin whereas the Lagergren model (R²=0.989) is that which describes best the adsorption of the Pb²⁺ ions in smectite. These results are confirmed besides by the values of the theoretical adsorbed quantities (Q_{e, calc}) and experimental (Q_{e,exp}) which are very close in the pseudo-second order model in the kaolin (13.35 mg/g and 12.89 mg/g respectively). These values are also very close in Lagergren model in smectite (26.66 mg/g and 23.94 mg/g). The adsorption process of lead (II) onto phosphate-modified kaolinitic clay made by Unuabonah *et al.* [16] follows the pseudo-second order reaction scheme as kaolin in this study. Sari *et al.* [17] in sorption of lead (II) onto Turkish kaolinitic clay and Olgun and Atar [9] in sorption of lead (II) onto clay mixture containing boron impurity obtained the same results by showing that adsorption of lead (II) on these clays followed pseudo-second order kinetic model. Speed constants of pseudo-first order of smectite and kaolin (0.112 min⁻¹ and 0.127 min⁻¹ respectively) are of the same order of magnitude. It is judicious to note that kaolin presents the highest speed constant (0.046 g/mg. min) obtained by the pseudo-second order kinetic model what explains besides why this model with a correlation coefficient of 0,999 is that which with the model of Elovich describes best the

adsorption of the Pb²⁺ ions in these materials more especially as the model of Elovich as for him presents the highest value of the desorption constant β of all studied materials (β=0.912 g/mg).

3.6. Macro and micro-pore diffusion

The adsorption mechanism of a sorbate onto activated carbon follows three steps: film diffusion, pore diffusion and intra-particle diffusion. The slowest of three steps controls the overall rate of the process. In a batch reactor pore diffusion and intra-particle diffusion are often the rate limiting step [21].

The intraparticle diffusion model of Weber and Morris shows that the diffusion is observed in the adsorption of lead (II) ions onto kaolin. As seen in the Fig. 13, this model presents two stages. The first stage is characteristic of the mass transfer taking place with boundary layer diffusion with a speed of about 3.8029 mg.g⁻¹.min^{-0,5}, this speed is much faster than that of the second phase (0.5479 mg.g⁻¹.min^{-0,5}) showing thus that it is this last stage which is the characteristic of the intraparticle diffusion which controls the adsorption of the Pb²⁺ ions in this kaolin. In smectite the two first stages (film and pore diffusion) are very fast and it is the intraparticle diffusion with a speed of about 4.2406 mg.g⁻¹.min^{-0,5} who is the limiting stage governing the adsorption of the Pb²⁺ ions in this material.

3.7. Adsorption mechanisms

The adsorption of lead (II) process onto smectite and kaolin is complex and involves more than one mechanism because of the mineralogical composition of the two clays essentially. Many authors [10,13-15,17] who made studies on kaolinitic clays and on illitic clays as respectively kaolin and smectite in this work showed that the adsorption of lead (II) onto these materials is made by electrochemical ion-exchange mechanism of selective adsorption ($x\text{Na}$ groups with Pb^{2+} , Ca^{2+} and Pb^{2+}) or by complexation reaction like reaction between amphoteric surface hydroxyls $-\text{SOH}$ and Pb^{2+} . That's why these reactions are expected in the sorption process of lead (II) onto smectite and kaolin. Moreover, Pb^{2+} ion is a softer cation so it is preferentially adsorbed on the softer basic sites with aluminol-phenol functional groups present on clay surfaces especially on kaolin.

Vereesh *et al.* [22] showed that the characteristics mineralogical and chemical grounds neutral and alkaline are favorable to a trapping of lead by precipitation or mineral coprecipitation what could explain while bringing back these results to the clays why smectite (pH=7) has tendency to adsorbing more lead compared to kaolin.

Alloway [23] showed that metals are fixed on clays by three mechanisms: the ions exchange, physical adsorption and chemical adsorption. This variety of mechanism explains the strong affinity of the Pb^{2+} ions with respect to two studied clays. The ions exchange particularly is the most important mechanism in clays. Indeed, smectite and kaolin in a natural way are good adsorbents of metal ions. It is in fact alumina silicates organized in layers in clays made of successive package of tetrahedral layers $(\text{Si}_2\text{O}_5)^{2-}$ and octahedral $(\text{Al}_2\text{OH}_4)^{2+}$. Isomorphous substitutions of silicon Si by alumina Al in the tetrahedral layer and of alumina by iron Fe and magnesium Mg in the octahedral layer will generate negative charges on the layers which will be compensated by the Pb^{2+} ions. Each zone of break of layers is electrically charged and taking into account the big number of breaks because clays are particles of small sizes ($2\mu\text{m}$) this is why strong chemical reactivity and physics vis a vis of lead (II) is observed in these two clay samples. These results are obviously confirmed by the great adsorption capacities and great adsorption percentages of adsorption (Tables-4-5) found previously for the two clays.

In addition Bittell and Miller [24] established an order of reactivity for the adsorption of lead on three types of argillaceous minerals: Kaolinite>illite>montmorillonite. Smectite and kaolin studied in this work have two of these three minerals (illite for smectite and kaolinite for kaolin (see XRD spectra on Figs.1-2). However Li and Li [25] show that clay rich in illite adsorbs more lead than a kaolinite and they allot this result to the differences of the surface charges between the kaolinite and the illite. This is why smectite rich in illite adsorbs much more Pb^{2+} ions than kaolin (rich in kaolinite).

4. Conclusion

The absorption of Pb^{2+} ions onto two clays smectite and kaolin was studied. Properties of the clays influence strongly the sorption process.

- SEM micrographs showed that the presence of pores particularly micropores enhances the adsorption capacity of the clay.
- Higher the specific surface area and porous volume greater the adsorption properties.

- The mineralogical composition showed that lead (II) is adsorbed onto smectite and kaolin by two mechanisms: electrochemical ion-exchanges and complexation reaction. Smectite rich in illite adsorbed more lead (II) than kaolin rich in kaolinite.

Environmental parameters such as pH, initial concentration of lead (II) solution and the contact time also influenced the sorption process:

- The increases of pH studied by increasing initial concentration make the lead (II) ions less available for the clays surfaces.
- The percentage removal of Pb^{2+} ions in the initial concentration decreases with the increase of initial Pb^{2+} ions concentration.
- The equilibrium is reached after 30 minutes for smectite and 40 minutes for kaolin.

The measure of the k_d -values showed that lead (II) is readily sorbed on the surfaces of the two clays but more onto smectite. The adsorption percentages at 60 ppm are respectively 46.63% and 24.45% for smectite and kaolin. Langmuir isotherm describes well the adsorption process on the two clays than Freundlich isotherm. The pseudo-second order and the Elovich kinetics models best described sorption kinetics on kaolin and the pseudo-first order on smectite. The intraparticle diffusion seems to be the rate limiting-step for the two adsorption processes.

Sorption technology on clay in general on smectite and kaolin particularly is shown to be a feasible alternative for removing lead (II) ions from wastes waters.

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6. Reference

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