Enhancing the adsorption of Pb(II) and Fe(II) in the reactor by the thermally treated alluvial clay from Far North Cameroon

Adjia Zangué H.1,2*, Nga B.2, Kamga R.2, Villiéras F.1 and Ebio Nko’o G.3

1Laboratoire Interdisciplinaire des Environnements Continentaux (LIEC) UMR 7360 CNRS-Université de Lorraine 15 Avenue du Charmois, 54500 Vandœuvre-lès-Nancy, France
2National School of Agro-Industrial Sciences (ENSAI) University of Ngaoundere B.P. 455 Adamaoua, Cameroon.
3Department of Chemistry, Faculty of Science (FS) University of Ngaoundere B.P. 454 Ngaoundere, Cameroon.

The objective of this work was to investigate the influence of the thermal treatment of alluvial clay on the adsorption capacity of Pb(II) and Fe(II) to reduce clogging during adsorption phenomenon. The chemical, X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM) and transmission electron microscopy (TEM) analysis of the alluvial clays reveal that the main mineral present is smectite, kaolinite and quartz. Cation exchange capacity (CEC) and specific surface area of the raw clay fraction are 62 meq/100 g and 104 m²/g respectively. The main oxides of alluvial clay fraction<50µm are SiO₂, Al₂O₃ and Fe₂O₃. The adsorbent used in this work is the alluvial clay, that after splitting has been thermally treated at 300°C and 600°C, the natural clay properties does not completely disappear until 300°C and 600°C. This study shows that the losses are about 3% for the heat treatment at 300°C (A300) and 5% for the heat treatment at 600°C (A600) after fractionation of Alluvial clays. The adsorption equilibrium is reached in five minutes, whatever the pH, temperature and the molar ratio of the solution. The pH is increased the removal increases as seen from plots of 2, 4 and 6 which gave removals as high as 92.15 μmol/g and 100.6 μmol/g to Pb(II) and 92.68 μmol/g and 110.5 μmol/g to Fe(II) respectively. The temperature is decreased the removal increases as seen from plots of 50°C, 40°C and 30°C which gave removals as high as 99.8 μmol/g and 100.3 μmol/g to Pb(II) and 98.9 μmol/g and 100.3 μmol/g to Fe(II) respectively. While, the adsorption capacity was increased as decreasing the temperature. So, it is recognized that adsorption mechanism should be physical adsorption. The adsorption process of Pb(II) and Fe(II) are best described by the second-order equation. However, the adsorption isotherms could be well fitted by the Freundlich equation, proves the surface heterogeneity of thermally treated Alluvial Clay.

Key words: Adsorption, agitated reactor, thermally treated alluvial clay, Cameroon.

INTRODUCTION

The pollution of water and/or soil, accidentally and/or voluntarily, by some chemicals of industrial origin (phenols, hydrocarbons, dyes ...) or agricultural (pesticides, fertilizers ...) constitutes a source of environmental degradation and is currently of particular interest internationally (Bouras, 2003; Demin et al., 2013).

Recent industrial revolution in central Africa as
Cameroon has enormously increased the industrial wastewater production which is highly contaminated with various types of heavy metals. Heavy metal contamination exists in waste effluents of different factories such as metal plating, mining operations, tanneries, ceramic painting, manufacturing paints, catalysts, alloy industries, galvanizing iron, polymer stabilizer, storage batteries manufacturing, pesticides, wood preservation, pigments factories and families cloths painting (Basso et al., 2002; Sundar et al., 2010; Arwidsson et al., 2010; Berthelot et al., 2008; Cao et al., 2008; Moon et al., 2010; Chrastny et al., 2010). Heavy metals have been acknowledged as potential health and environmentally hazardous materials. Many studies have shown that these metals are toxic even at low concentrations. The presence of these toxic metals can in turn, cause accumulative poisoning, destroy liver, cancer and brain damage when found above the tolerance level (Arif et al., 2015; Geier et al., 2015; Carneiro et al., 2014; Chen et al., 2012; Ilyin et al., 2010; Bridges and Zalups, 2010; Ilyin et al., 2002, 2003; CACAR, 2003; Carretero et al., 2002; Chang, 1977). Additionally, another problem in our study area is the presence of iron on the soil and this iron migrated in water process. Presently, many techniques such as chemical precipitation, extraction, reverse osmosis and adsorption are being used for the removal of heavy metals from wastewater. Adsorption technique is an economical process especially using low cost adsorbents. Many investigators have evaluated natural clay and the date pits as low-cost adsorbents due to their adsorption properties for heavy metals including cobalt, lead, cadmium, zinc and chromium ions (Ahmad et al., 2011, 2018; Sameeh et al., 2017; Ahmad et al., 2019). In contrast, there are very few studies on the mineralogy and use of clays from vertisol of the northern region of Cameroon. None of the above studies are dealing with alluvial clay of the far north region of Cameroon. In fact, Adjia et al. (2014) discovered new adsorbent, alluvial clay as alternative solution to resolve waste water problem.

Lead and iron are considered dangerous micropollutants. In fact, Lead is the heavy metal and Iron is presented on the littoral soil, affects processing water, and decreases by this fact the rentability of the industries in this economical area of Cameroon.

The toxicity affected by these heavy metals is considered high even in trace amounts (IARC, 1992; Curren et al., 2015). Given the variable quality of the contaminated water and the harmful effects of pollution, this metal as micropollutant is reduced by adsorption on the alluvial clay. Using alluvial clays as adsorbents is of interest in the removal of pollutants. This is justified by the importance of the surface developed by this material, by the presence of negative charges on the surface, by the possibility of exchange of the cations and by a wide availability in nature (Adjia et al., 2014).

However, many studies showed that, during the adsorption phenomenon in the reactor we have the clogging problem (Vishal et al., 2013). The aim of this work is to investigate the influence of heat treatment of a Alluvial clay on its adsorption capacity of Pb (II) and Fe (II) in the reactor.

**MATERIALS AND METHODS**

**Alluvial clay materials**

**Study area and sampling**

The soil samples were taken in a dry river bed situated between the towns of Maroua and Kaele in the far-north region of Cameroon (Picture 1). The system coordinates of this area is 10°02.883N and 014°23.084E. The climate is tropical-dry, characterized by 7-8 months of dry season and 4-5 months of wet season. The mean annual rainfall and temperature in the area is 800 mm and 28.5°C, respectively. During the wet season, the rivers (locally call Mayo) contain running water while in the dry season there is almost no water. The soil depth during the sampling is 99 cm (Adjia et al., 2013, 2014).These soil samples were packaged in plastic packaging.

The soil fraction <50 μm (A50)

In this study, we focused on the size fraction <50 μm. The soil aggregate is pulverized in a mortar and then homogenized. About 1 kg of this sample is soaked in 2 L of distilled water for 4 h. This mixture is homogenized by subjecting to wet sieving with a 50-μm mesh sieve. The water is then removed by drying at 105°C in an oven for 24 h. The solid obtained was treated with 5% hydrogen peroxide solution to eliminate organic matter. The dried fraction is sprayed in an Agate mortar; the powder obtained is weighed and stored in a sealed jar; and the clay fraction <2 μm (A02) was extracted by sedimentation. However, especially in this work, the resulting mixture was then sieved over 50-μm (A50) mesh sieve.

Mineralogy and physicochemical properties

**X-ray diffraction (XRD):** The X-ray diffraction (XRD) data were obtained using a DB Bruker diffractometer with CoKα radiation (λ=1.789 Å). Spectra were recorded on oriented and unoriented samples. The detection limit for a given crystalline phase is estimated at around 1% in mass. Ethylene glycol and heat treatments (550°C) were used to provide additional information essential for the identification of clay minerals.

**Fourier Transform Infra Red (FTIR):** Infrared spectra were recorded using an IFS 55 Bruker Fourier transform IR spectrometer equipped with an MCT detector (6000 to 600 cm⁻¹) cooled at 77K and in diffuse reflectance (Harrick attachment) mode. The amount of clay was 70 mg dispersed in 370 mg KBr.
Scanning and transmission electron microscopy: TEM observations were conducted with a Philips CM20 microscope equipped with an EDS detector. Secondary and backscattering SEM observations were carried out on a Hitachi 2500 LB SE microscope equipped with a Kevek Delta EDS spectrometer. SEM was used to assist in the identification of individual accessory minerals incorporated in the clay samples by comparing their morphological characteristics with their elemental compositions.

Chemical analyses: These were performed on the two clay fractions. The major elements were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES), whereas trace elements and rare earths elements were determined by inductively coupled plasma mass spectrometry (ICP-MS).

Cation exchange capacities (CEC): These were measured using cobaltihexammine [Co(NH₃)₆Cl₂] as exchangeable ions. The amount of cobaltihexammine fixed by the solid phase was determined from concentration measurements using UV-vis spectroscopy. The displaced cations were determined by atomic absorption spectrometry (Perkin-Elmer 1100B). The equilibrium pHs of clay suspensions were determined using a standard LPH 330 T electrode.

Textural properties: Nitrogen adsorption-desorption isotherms at 77K were recorded on a step-by-step automatic home-built set up. Pressures were measured using 0-1000 Pa and 0-100.000 Pa Baratron-type pressure sensors provided by Edwards. The nitrogen saturation pressure was recorded in situ using an independent 0-100.000 Pa Baratron-type pressure sensor provided by Edwards. Prior to adsorption, the samples were outgassed overnight at 120°C and under residual pressure of 0.01 Pa. Nitrogen N55 (purity > 99.9995%) used for experiments was provided by alphagaz (France). Specific surface areas (SSA) were determined from adsorption data by applying the Brunauer-Emmet-Teller (BET) equation and using 16.3Å² for the cross sectional area of nitrogen. In the present study, error in the determination of the SSA was estimated as +/- 1 m²/g. Micropores volumes and non-microporous surface areas were obtained using the t-plot method proposed by De Boer et al. (1996). Pore size distributions were calculated on the desorption branch using the Barrett-Joyner-Halenda method, assuming slit-shaped pores.

Heat treatment

The treatment is carried out using a muffle furnace. It consists in weighing the crucible empty, then putting 159.94 g of alluvial clay fraction in the crucible, weighed, and then the sample was introduced into the oven at different temperatures from room temperature (25±1°C) to the temperature set for 40 min at 300°C and 70 min at 600°C. Finally, it was allowed to cool and the samples weighed again.

Experimental procedures

Lead salts (Pb(NO₃)₂) and Mohr salt (Fe(NH₄)₂(SO₄)₂·6H₂O) are used for the preparation solutions, using waste water conditions. All experiments were carried out at pH 7.0 (except when the effect of pH was studied). The pH of each solution was adjusted to the desired value by addition of dilute HCl or NaOH solutions.
Preparation of solutions and Adsorption phenomenon

The initial lead solution at 4826 μmol/L was prepared by dissolving 0.81g of lead nitrate salt (Pb(NO₃)₂) hydrated in 500ml of distilled water. The resulting solution was stored in a one-liter flask. This solution has been diluted to provide solutions of desired concentrations during adsorption.

The initial solution of 17851 μmol/L Iron was prepared by dissolving 3.5 g of hydrated Mohr salt (Fe(SO₄)₂(NH₄)₂(SO₄)₂·6H₂O) in 500 ml of distilled water. The resulting solution was stored in a one-liter flask.

For the adsorption experiments, 25 ml of lead nitrate solution (289.6 μmol/L) and Mohr salt at a concentration of 1071.4 μmol/L are introduced into a 50-ml series of Erlenmeyer flasks. The whole solution is kept at ambient temperature (25 ±1°C) and stirred with a water bath at a constant speed of 120 rpm. Subsequently, 0.25 g of alluvial clay of each sample is introduced into each Erlenmeyer flask. These are then stirred at approximately 60 rpm at constant temperature for a period of one hour. At each time interval, the contents of the Erlenmeyer flask are filtered on Whatman N°1 filter paper. The optical density read at the visible spectrophotometer is in the range C.

Equilibrium adsorption was determined using the isotherms of Langmuir and Freundlich.

Effect of temperature: To measure the influence of temperature, we will have three temperatures between 30 and 50°C, initial concentration, adsorbent and normal pH. Temperature has two major effects on the adsorption process.

Modeling adsorption kinetics: Adsorption kinetics were studied using the pseudo-first-order, pseudo-second-order and intraparticular diffusion equations.

i) Kinetic model of pseudo-first order: The velocity equation of the pseudo-first-order kinetic model is given by the relation:

\[ q_t = q_e \left(1 - e^{-kt} \right) \]

Where, \( q_e \) is the amount of the metal adsorbed; \( q_0 \) is the initial concentration of the solution (μmol/L); \( k \) is the pseudo-first order rate constant. Representing the log \( q_t - q_e \) = f(t) function, we obtain a straight line of slope \( k \) and an intercept of log \( q_e \) (Harouna et al., 2015).

ii) Kinetic model of pseudo-second order: The pseudo-second-order kinetic model can be represented in the following form:

\[ \frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{t}{q_e} \]

Where \( q_e \) and \( q_t \) are respectively the relative quantities adsorbed at equilibrium and at time t, \( k_2 \) is the pseudo-second-order rate constant (Harouna et al., 2015).

iii) Kinetic model of intra particle diffusion: The intraparticular diffusion model can be represented by the equation:

\[ q_t = k_{int}\sqrt{t} + C \]

Where \( q_t \) is the relative amount of adsorbed Lead and Iron at time t, \( k_{int} \) is the intraparticular diffusion constant and C is a constant (Reddy et al., 2010). The regression of the function \( q_t = f(\sqrt{t}) \), makes it possible to obtain a line of slope \( k_{int} \) and ordinate at the origin C.

Modeling adsorption isotherms: The adsorption capacity was determined using the isotherms of Langmuir and Freundlich.

i) Langmuir model: The theory proposed by Langmuir is based on a homogenous distribution of the adsorption sites. The Langmuir isotherm can be represented by the equation:

\[ q_e = \frac{aK_FC_c}{1 + aC_c} \]

Where \( C_c \) is the residual relative amount at the adsorption equilibrium, \( q_e \) the relative amount of the adsorbed Lead and Iron per gram of adsorbent has the adsorbed amount for the monolayer and \( K \) the equilibrium adsorption constant (Domga et al., 2015).

ii) Freundlich model: The simple and empirical model of Freundlich is the second most commonly used model. It is considered that it applies to many cases, especially in the case of an adsorbent with a heterogeneous adsorption surface (energetically different adsorption sites).

\[ q_e = K_FC_c^{1/n} \]

The linear expression of the Freundlich equation is obtained by taking the logarithm of the equation:

\[ \ln q_e = \ln K_F + \frac{1}{n} \ln C_c \]

Where \( K_F \) and \( n \) are the constants respectively reflecting the measurement of the adsorption capacity and the adsorbent-adsorbate affinity (Harouna et al., 2015).

RESULTS AND DISCUSSION

Mineralogy and physicochemical properties

X-ray diffraction

XRD patterns of alluvial clay samples show that it consists predominantly in smectite, kaolinite and quartz, with accessory minerals such as anatase, microcline, albite and rutile (Figure 1a). Results of the ethylene glycol test on oriented clay fraction showed the characteristic displacement of the basal peak of smectite from 15.2 to 18.3 Å (Figure 1b). The usual displacement of the smectite from 15.2 to 10.1 Å on heating at 550°C is also observed. All the vertisol profiles in this area showed a similar mineralogical composition; however, Adjia et al. (2013, 2014) found that most of the smectite minerals of the vertisol soil of this zone are mixtures of montmorillonite and beidellite. The spectra of the A50
fraction show a well-defined peak of quartz indicating a high amount of quartz in this sample. On the contrary, the clay fraction only presents very few amount of quartz.

**Infrared spectroscopy**

The infrared spectra of the two clays fractions are presented in Figure 2. The two spectra have almost the same feature. IR analysis confirms that smectite and kaolinite are the main mineral present in our clay samples. The broad band at 3390 cm\(^{-1}\) is usually attributed to the adsorbed water at the interlayer of smectite clays. The band at 1612 cm\(^{-1}\) is also attributed to smectite interlayer water. The band at 3698 cm\(^{-1}\) is assigned to the OH stretching vibration of kaolinite, whereas the band at 3620 cm\(^{-1}\) is characteristic of the OH stretching of kaolinite and of Al\(_2\)O\(_3\)OH or AlMgOH groups.
of smectite. In addition, IR analysis shows the absence of calcium or magnesium carbonates and of organic matter in the studied samples.

**Scanning and transmission electron microscopy**

SEM observation on a polish slide of A50 fraction shows large aggregates and small particles dispersed over the entire matrix (Figure 3a). SEM with EDX analysis of the aggregates reveal the presence of smectite [A]: (Si/Al=0.60), of microcline [B]: (Si/Al=2.8 and 3), of quartz [C]: (Al=0), of interstratified [D]: (Si/Al=1.6) and of kaolinite [E]: (Si/Al=2). Those minerals have currently been identified from XRD and IR analyses. The SEM images of A50 powder shows the usual cluster of rose...

Figure 2. Infrared spectrum of the Alluvial Clay A02 and A50.

Figure 3. Scanning electron photomicrograph (SEM) and TEM micrograph of alluvial clayey fraction, showing typical texture. 3a) SEM A50 (polished slide of clay embedded in resins); 3b) SEM A50 (powder); 3c) TEM A02. Minerals identification is derived from EDX analyses.
shaped aggregates of smectite particles (Figure 3b). TEM-EDX analysis confirms the presence of kaolinite and smectite; and also reveals the additional presence of quartz, feldspar and iron oxy-hydroxides as minor phases (Figure 3c) (Adjia et al., 2013).

**Chemical analyses**

The major element composition of the alluvial clay fraction is presented in the Table 1 below. The main oxides of alluvial clay fraction <50 µm are SiO₂, Al₂O₃ and Fe₂O₃. The high amount of SiO₂ in the alluvial clay fraction<50 µm is related to its high content in quartz as compared to the alluvial clay fraction. Small amount of MnO, MgO, CaO, Na₂O, K₂O, TiO₂ and P₂O₅ are also found in the two samples. This implied that Mg²⁺, Ca²⁺ and Na⁺ are exchangeable cations of the alluvial clays samples (Adjia et al., 2013).

**Physico-chemical characteristics of the alluvial clay**

The cation exchange capacity (CEC) values measured from variation in concentration of cobaltihexamine match those deduced from the chemical analysis of exchangeable cation for all the samples described herein. This confirms the absence of soluble phases in the studied fraction. The CEC of the clay fraction (Table 2) lie between the values reported in the literature for smectites, that is, 60 to 150 meq/100 g (Adjia et al., 2014). The lower CEC value for A50 fraction compared to clay fraction correlates with its lower content in clays. Indeed, the CEC ratio between A50 and A02 is 0.54, in good agreement with the 57% of clays in A50. From the analyses of the cations exchanged with cobaltihexamine, it can be concluded that around 2/3 of the layer charge is compensated by divalent cations (Ca²⁺ and Mg²⁺) (Adjia et al., 2013).

**Textural**

The adsorption-desorption isotherms on the two samples reported in Figure 4 are typical of clay materials containing smectites (Neaman et al., 2003). Numerical values deduced from the adsorption and desorption isotherm are given in Table 3. The difference in the specific surface areas (SSA) of A02 and A50 fractions can be attributed to their quartz content. In fact, A50 fraction contains a large amount of quartz, and quartz particles present low specific surface areas compared to clays. Indeed, the 0.54 SSA ratio between A50 and A02 samples is also consistent with CEC and clay content of A50 showing that sandy fraction of A50 has no surface area. Microporosity represent about 20% of the total surface area and can be assigned to clay layers organisation as generally observed in the case of swelling clays with divalent exchangeable cations (Adjia et al., 2014).

**Influence of pH**

It appears from Figure 5 that the kinetics of adsorption kinetics of Pb(II) are all the same pace. The balance is reached in less than 5 min, implying that equilibrium had been reached. The amount of Pb(II) adsorbed increases with pH. The amount adsorbed at equilibrium is of the same order for the two samples. The type of thermally

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**Table 1.** Chemical analysis of major elements on a sandy fraction <50 µm (A50) and clayey fraction< 2 µm (A02).

<table>
<thead>
<tr>
<th>Sample (%)</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>MnO</th>
<th>MgO</th>
<th>CaO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>TiO₂</th>
<th>P₂O₅</th>
<th>LOI</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>A02</td>
<td>46.37</td>
<td>22.88</td>
<td>9.21</td>
<td>0.04</td>
<td>1.27</td>
<td>0.87</td>
<td>0.56</td>
<td>1.05</td>
<td>1.26</td>
<td>0.08</td>
<td>16.5</td>
<td>100.0</td>
</tr>
<tr>
<td>A50</td>
<td>60.66</td>
<td>17.04</td>
<td>5.88</td>
<td>0.09</td>
<td>0.75</td>
<td>0.77</td>
<td>0.94</td>
<td>3.18</td>
<td>1.34</td>
<td>0.06</td>
<td>9.45</td>
<td>100.1</td>
</tr>
</tbody>
</table>

Note: LOI: loss on ignition.

**Table 2.** Equilibrium pH, cation exchange capacities (CEC), and exchangeable cations of the clay fraction on a sandy fraction <50 µm (A50) and clayey fraction< 2 µm (A02).

<table>
<thead>
<tr>
<th>Samples</th>
<th>pH±0.1</th>
<th>CEC (chem) meq/100 g ± 5</th>
<th>CEC (UV) meq/100 g ±5</th>
<th>Na⁺ (meq/100 g)± 2</th>
<th>K⁺ (meq/100 g)± 1</th>
<th>Ca²⁺ (meq/100 g)± 2</th>
<th>Mg²⁺ (meq/100 g) ± 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>A02</td>
<td>9.2</td>
<td>58</td>
<td>62</td>
<td>14.8</td>
<td>1.0</td>
<td>29.2</td>
<td>13.0</td>
</tr>
<tr>
<td>A50</td>
<td>9.5</td>
<td>31</td>
<td>34</td>
<td>6.3</td>
<td>0.6</td>
<td>15.8</td>
<td>6.3</td>
</tr>
</tbody>
</table>

Note: Chem: derived from chemical analysis of displaced cations. UV: derived from the measurement of cobaltihexamine concentrations by UV-visible spectroscopy.
Figure 4. Nitrogen adsorption and desorption isotherms at 77K. For a) clay fraction (A02) and sandy fraction (A50) ●: A02 ; ◊: A50.

Table 3. Textural parameters deduced from N₂ adsorption desorption isotherms (SSA: specific surface area) on a sandy fraction <50 µm (A50) and clayey fraction <2 µm (A02).

<table>
<thead>
<tr>
<th>Samples</th>
<th>BET C constant</th>
<th>BET SSA (m²/g) ±1</th>
<th>Non Microporous surface area (m²/g) ±1</th>
<th>Microporous equivalent surface area (m²/g) ±1</th>
<th>Microporous Volume (cm³/g) ± 0.0003</th>
</tr>
</thead>
<tbody>
<tr>
<td>A02</td>
<td>215</td>
<td>103</td>
<td>82</td>
<td>26</td>
<td>0.0091</td>
</tr>
<tr>
<td>A50</td>
<td>337</td>
<td>56</td>
<td>44</td>
<td>15</td>
<td>0.0053</td>
</tr>
</tbody>
</table>

Note: SSA: specific surface area

treatment of alluvial clay and salts solutions do not influence this adsorption. However, as the pH is increased, the removal increases as seen from plots of 2, 4 and 6 which gave removals as high as 92.15 and 100.6 μmol/g to Pb(II) as well as 92.68 and 110.5 μmol/g to Fe(II) respectively (Figures 5 and 6). As shown, the maximum biosorption capacity was reached at pH 6 with 100.6 μmol/g to Pb(II) and 110.5 μmol/g to Fe(II), respectively for lead and iron concentration.

As for Pb(II) and Fe(II) in Figure 6, adsorption equilibrium is rapidly reached (92.15 and 92.68 μmol/g). However, the influence of the pH is less marked, with the adsorption done in the same way with the pH 2, 4 and 4. At pH values higher than 7, Fe(II) precipitation occurred. One notes an increase of the quantities adsorbed by 11% when one passes from the pH 4 until the pH 6.

The alluvial clays are known to possess a negative surface charge in solution. As pH changes, surface charge also changes, and the sorption of charged species is affected (attraction between the positively charged metal ion and the negatively charged clay surface). The effect of pH can be explained in terms of pHzpc (zero point of charge) of the adsorbent. Below this pHzpc, the surface charge of the adsorbent is positive. An increase in pH above pHzpc shows a slight increase in adsorption in which the surface of the adsorbent is negatively charged and the sorbate species are still positively charged. The increasing electrostatic attraction...
between positive sorbate species and adsorbent particles would lead to increased adsorption of metal ions (Kadirvelu et al., 2001).

**Influence of temperature**

As the temperature is decreased the removal increases as seen from plots of 50, 40 and 30°C which gave removals as high as 99.8 and 100.3 μmol/g to Pb(II) as well as 98.9 and 100.3 μmol/g to Fe(II) respectively. It can be concluded from Figures 7 and 8 that decreasing the temperature increases adsorption. The maximum adsorptions of Pb(II) and Fe(II) ions on thermally treated alluvial clay were found at T= 30°C “to A300 and A600 of Pb(II)” and T= 30°C “to A300 and A600 of Fe(II)”, respectively. Consequently, it is clear that adsorption equilibrium is not a thermo-dependent process, because the alluvial clay is thermally treated. This is mainly because of increased surface activity suggesting that adsorption between metal ion and alluvial clay is an exothermic process (Yasemin and Zübeyde, 2006; Johnson, 1990). Meanwhile, the adsorption capacity was increased as the temperature decreases. So, it should be recognized that the adsorption mechanism is physical.

**Modeling the kinetics of adsorption**

This helps to investigate the possible mechanisms involved in the adsorption of theoretical Pb(II) and Fe(II) intraparticle diffusion, pseudo-first order and pseudo-second order.

Intraparticular and pseudo-first order diffusion models are not applicable for the explanation of the adsorption of Pb(II) and Fe(II) by our thermally treated alluvial clays at 300 and 600°C given the low values of the R² coefficients for these models (Table 4). The coefficients of determination R² for the pseudo-second-order kinetic model are close to 1 regardless of the alluvial clay
Figure 6. Effect of pH on Fe(II) adsorption kinetics by thermally treated Alluvial clay at a) 300°C (A300) and b) 600°C (A600): pH=2; pH=4 and pH=6.

Modeling isothermal adsorption

The Langmuir and Freundlich models are often used to describe equilibrium sorption isotherms. The most widely used Langmuir equation, which is valid for monolayer sorption on to a surface with a finite number of identical sites, is given by Equation 5. The widely used empirical Freundlich equation based on sorption on a heterogeneous surface is given by Equation 6. The calculated results of the Langmuir and Freundlich isotherm constants are given in Table 5. It is found that the adsorptions of Pb(II) and Fe(II) on thermally treated alluvial clay correlated well (R > 0.99) with the Langmuir equation as compared to the Freundlich equation under the concentration range studied. The essential features of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, \( R_L \), which is used to predict if an adsorption system is “favourable” or “unfavourable”. The separation factor, \( R_L \) is defined by:

\[
R_L = \frac{1}{1+bc_0}
\]  

where \( C_0 \) is the initial Pb(II) or Fe(III) concentration (ppm) and \( b \) is the Langmuir adsorption equilibrium constant (ml.mg\(^{-1}\)). Table 6 lists the calculated results. Based on the effect of separation factor on isotherm shape, the \( R_L \)
**Figure 7.** Effect of temperature on the adsorption kinetics of Pb(II) by thermally treated Alluvial clay at a) 300 °C (A300) and b) 600 °C (A600): T = 30°C, T = 40°C and T = 50°C.

**Figure 8.** Effect of temperature on Fe(II) adsorption kinetics by thermally treated Alluvial clay at a) 300°C (A300) and b) 600°C (A600): T = 30°C, T = 40°C and T = 50°C.
values are in the range of $0 < R_L < 1$, which indicates that the adsorptions of Pb(II) and Fe(II) on thermally treated alluvial clay are favourable. Thus, thermally treated alluvial clays are favourable adsorbers. Indeed, the Langmuir model indicates that we have a homogeneous distribution of adsorption sites while the model shows that our adsorbent has a surface heterogeneity.

**Conclusion**

In this study, enhancing the adsorption of Pb(II) and Fe(II) by the thermally treated alluvial clay from far north Cameroon in the reactor was examined, including equilibrium and kinetic studies. In a view to evaluate their potential use as adsorbent for wastewater treatment, the mineralogical and physico-chemical properties of alluvial clays from far north region of Cameroon has been determined. The alluvial clays reveal that the main mineral present is smectite, kaolinite and quartz. Cation exchange capacity (CEC) and specific surface area of the raw clay fraction are 62 meq/100 g and 104 m$^2$/g respectively. The main oxides of alluvial clay fraction<50 μm are SiO$_2$, Al$_2$O$_3$ and Fe$_2$O$_3$. The overall formula of the clay mineral which was established are: smectite, $[Si_{3.42}Al_{0.58}]_0[Al_{0.87}Fe_{0.96}Mg_{0.17}]_{octa}O_{10}(OH)_2(C^+)_{0.75}$; and kaolinite, $Si_{2}Al_{1.95}Fe_{0.05}O_{10}$(OH)$_4$.

As the pH is increased, the removal increases as seen from plots of 2, 4 and 6 which gave removals as high as 92.15 and 100.6 μmol/g to Pb(II) and 92.68 and 110.5 μmol/g to Fe(II) respectively. As the temperature is decreased the removal increases as seen from plots of 50, 40 and 30°C which gave removals as high as 99.8 and 100.3 μmol/g to Pb(II) and 98.9 and 100.3 μmol/g to Fe(II) respectively. Meanwhile, the adsorption capacity was increased as the temperature decreases. So, it should be recognized that adsorption mechanism is physical. The adsorption process of Pb(II) and Fe(II) are best described by the second-order equation. In our case, the second-order equation correlates well to the adsorption studies. It is more likely to predict that the adsorption behaviour may involve valency forces through sharing of electrons between transition metal cations and adsorbent. However, the adsorption isotherms could be well fitted by the Freundlich equation, which proves the surface heterogeneity of thermally treated alluvial clay. The $R_L$ values are in the range of $0 < R_L < 1$, which indicates that the adsorptions of Pb(II) and Fe(II) on thermally treated alluvial clay are favourable. The clogging is not the problem during adsorption studies.}

**CONFLICT OF INTERESTS**

The authors have not declared any conflict of interests.
ACKNOWLEDGEMENTS

The authors are grateful to all members and teachers of the Applied Chemistry Laboratory ENSAI, Department of Chemistry (FS) for the efforts made towards the success of this work.

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