A Comparative Study of the Linear and Non-Linear Methods for Determination of the Optimum Equilibrium Isotherm for Adsorption of Pb^{2+} Ions onto Algerian Treated Clay

Benmessaoud, Atallah; Nibou, Djamel*[+]; Mekatel, El Hadj; Amokrane, Samira

Laboratory of Materials Technology, University of Science and Technology Houari Boumediene, B.P. 32, El-Alia, Bab-Ezzouar, Algiers, ALGERIA

ABSTRACT: *The adsorption equilibrium isotherms of lead from aqueous solutions onto treated clay were studied and modeled. The ability of clay to remove Pb^{2+} ions from aqueous solutions has been studied at different operating conditions: contact time (5-90 min), adsorbent dosage (1-4 g/L), initial ion concentration (10 - 200 mg/L) and pH solution (1 - 11) and temperature (298 - 333 K). The maximum uptake (98.%) is obtained under the optimum conditions: pH ∼ 7 and adsorbent dose of 2.5 g/L for an initial concentration of 10 mg/L at 298 K. In order to determine the best-fit isotherm, the experimental equilibrium data were analyzed using some adsorption isotherm models with two-parameters as Langmuir, Freundlich, Temkin, Elovich and Dubinin-Radushkevich, and three-parameters as Langmuir-Freundlich, Redlich-Peterson, Sips, Fritz-Schlender, and Toth. Models with four-parameters as Fritz-Schlunder and Baudu and with five-parameters as Fritz-Schlunder were also used. A comparison of linear and non-linear regression methods for predicting the optimum isotherms was made using the experimental adsorption equilibrium data of Pb^{2+} ions onto treated clay. The following error analysis methods were used, the coefficient of determination R^2, the sum of the squares of the errors, the sum of the absolute errors, the average relative error, the Mean Square Error, and the Root Mean Square Error. The error values indicated that the non-linear method is a better way to obtain the isotherm parameters describing the Pb^{2+} ions adsorption onto the clay. The comparison between different models shows that the Fritz-Schlünder model with five-parameters was more suitable to describe the equilibrium data. The kinetics data of batch interaction was also analyzed with various kinetic models. It was found that the pseudo-second-order model using the non-linear regression method predicted best the experimental data.*

KEYWORDS: *Adsorption; treated clay; Pb^{2+} ions; isotherms; linear and non-linear regression; Kinetic.*

INTRODUCTION

Nowadays heavy metals are among the most important pollutants in source and treated water and are becoming a severe public health problem. Industrial and municipal wastewaters frequently contain metal ions. Industrial waste constitutes the major source of various kinds of metal pollution in natural water [1–3]. The heavy

***** *To whom correspondence should be addressed.*
+ E-mail: dnibou@Yahoo.fr
1021-9986/2020/3/153-171 11/$/6.01

metal ions are stable and persistent environmental contaminants, since they cannot be degraded and destroyed. These metal ions can be harmful to aquatic life, and water contaminated by toxic metal ions remains a serious public health problem for human health. Lead (Pb) is one of the major environmental pollutants because of its presence in automobile fuel and subsequent emission into the atmosphere in the exhaust gases [3-5]. Moreover, it penetrates to the water environment through effluents from lead smelters, battery manufacturers, paper and pulp industries, and ammunition industries [6-7]. There are many different methods for treating wastewaters. Current methods for wastewater treatment include precipitation, coagulation/flotation, sedimentation, flotation, filtration, membrane processes, electrochemical techniques, ion exchange, biological processes, chemical reactions, and adsorption [8-9]. Adsorption is one of the important procedures for the removal of the heavy metals from the environment. Ion exchange and adsorption mechanisms of clay minerals have been used to remove different environmental contaminants [10-13]. The main properties of the natural adsorbents are strong affinity and high loading capacity for the removal of heavy metals. Natural clay minerals are used as adsorbents for the removal of heavy metals due to their structural properties such as high cation exchange capacity, high surface area and high adsorption/absorption. These are advanced functional materials of significant potential for environmental protection [14-15]. However, the adsorption capacity and selectivity of natural clay are limited. Thus, a systematic modification of the surface is essential to increase the capacity and the yield the elimination of organic and inorganic compounds. Various chemical methods exist for the modification of clays, treatments with cationic surfactants [16], including acid attack [17], NaCl activation [18], thermal treatment [19], binding of inorganic and organic anions, grafting of organic compounds [20] and supported semiconductors [21-22]. Among these methods, the treatment by NaCl is simple and low cost. In this respect, treated clay find industrial applications as bleaching earth, catalysts and catalyst supports and NaCl activation is a useful to modify the clay.

The search for the best fit adsorption isotherm using the linear regression method is the widely used technique to evaluate the model parameters and to determine the best fitting model. However, depending on the way of the isotherm equation linearization, the distribution of error changes either the worst or the best [23-25]. So, the method of non-linear regression is used by several researchers to determine the adsorption isotherm parameters [26-31]. It is based on the minimization of error distribution between the experimental data and the predicted isotherm. Several error functions are used to evaluate isotherm data. The most common error functions used are: The coefficient of determination R^2, Sum of the Errors Squared (SSE), Sum of the Absolute Errors (SAE), the Average Relative Error (ARE), the Mean Square Error (MSE), the Root Mean Square Error (RMSE) [32-33].

The aim of the present work is to investigate the ability of clay to remove lead ions from aqueous solution. Batch adsorption experiments will be applied. The effect of various parameters on the adsorption process such as the effects of contact time, pH, initial metal ion concentrations, dose of adsorbent and temperature will be investigated. Isotherm models with two parameters (Langmuir, Freundlich, Temkin, Elovich and Dubinin-Radushkevich), with three parameters (Langmuir–Freundlich, Redlich–Peterson, Sips, Fritz–Schlender, and Toth), with four parameters (Fritz–Schlunder, and Baudu) and with five parameters (Fritz–Schlunder) were used to fit the experimental data and to determine the best-fit isotherm.

EXPERIMENTAL SECTION

Chemicals and materials

All chemicals used in the experimental study were of analytical quality. Pb $(NO_3)_2$ (≥ 99% purity), HNO_3 (65% purity), HCl (37% purity), NaCl (extra pure), KNO_3 (≥ 99.5% purity) and NaOH (98% purity) were purchased from SIGMA ALDRICH company. Distilled water (0.8 MΩ cm) was used for preparing all solutions.

Adsorbent preparation

The natural clay used in the present study was collected from a quarry in north east of the Laghouat region (N: 33°54'51.34", E: 2°37'3.72" and A: 905m). This clay is crushed and sieved to obtain fractions smaller than 100 μm and then washed with distilled water for 24 h and then decanted and dried. Then, this clay undergoes a cation exchange step using a solution of NaCl (1M) with a contact time of 3 days. This operation is repeated

3 times before undergoing several washes with distilled water and then dried in the oven at 60 °C. for 24 h.

Characterization

The X-ray diffraction (XRD) patterns of the adsorbent were obtained using a Philips (XPERT-PRO X, Germany) ray diffraction instrument with filtered Cu Kα radiation (n=1.5418 Å) operated at 45 kV and 40 mA. The morphology of clay sample was observed by Scanning Electronic Microscope (SEM) using a JEOL 6360 (Japan) instrument equipped with an Energy Dispersive Spectroscopy (EDS) analyzer. The sample was coated with a thin film of carbon. The FTIR analysis was carried out using Perkin Elmer Spectrum equipment (Version 10.03.06, Germany). The remaining Pb^{2+} ions concentrations in the aqueous phase were determined using an Atomic Absorption Spectrometer (ANALYTIC JENA, NOVAA 350). The point of zero charge (pH_{PZC}) of the treated clay was measured for understanding the adsorption mechanism of Pb^{2+} ions. The method reported by *Boudechiche et al.* [34] was used for this purpose.

Batch experiments

Lead solutions of different concentrations were made by dilution of 500 mg/L stock solution prepared from analytical grade of $Pb(NO_3)_2$. Adsorption was performed in batch experiments where 100 mL of aqueous solutions of Pb^{2+} ions were mixed with 0.2 g of adsorbent in conical flasks. The pH of each suspension was adjusted in the range of 1 to 11 by adding HNO_3 (0.1 N) or NaOH (0.1 N) solutions and monitored with pH meter. The mixed solutions were shaken in optima mechanical shaker at 150 rpm and 25 °C for a given time. After the contact time was completed, solution and clay were separated by a filter paper (0.45 μm cellulose syringe filter). In order to evaluate the amount of lead ions retained per unit mass of treated clay, the adsorption capacity was calculated using the following equation:

$$q_e = (c_o - c_e)\frac{v}{m} \quad (1)$$

Where q_e is the amount of Pb^{2+} ions adsorbed (mg/g), C_o is the initial Pb^{2+} ions concentration (mg/L), C_e is the equilibrium Pb^{2+} ions concentration (mg/L), V is the volume of the solution (L) and m is the weight of the adsorbent (g).

Theoretical background

The equations of isotherm models and their linear and non-linear forms are regrouped in Table 1. The Langmuir model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface [34]. The Langmuir parameters are defined as follow: qe is the amount of solute adsorbed per unit weight of adsorbent at equilibrium (mg/g), C_e is the equilibrium concentration of the solute in the bulk solution (mg/L), q_{mL} is the maximum adsorption capacity (mg/g) and K_L is the constant related to the free energy of adsorption (L/mg).

The Freundlich expression is an exponential equation and therefore, assumes that as the adsorbate concentration increases, the concentration of adsorbate on the adsorbent surface also increases [35]. The linear form of the Freundlich isotherm is shown in Table 1 where K_F is a constant indicative of the relative adsorption capacity of the adsorbent ($mg^{1-(1/n)}\ L^{1/n}\ g^{-1}$) and n is a constant indicative of the intensity of the adsorption.

The *Temkin* [36] isotherm equation assumes that the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent-adsorbate interactions, and that the adsorption is characterized by a uniform distribution of the binding energies, up to some maximum binding energy. The linear form of the Temkin isotherm is shown in Table 1 where B_T (B_T = RT/b) is related to heat of adsorption (J/mol), R is the gas constant (8,314 J/mol K), T is the absolute temperature (K) and K_T is the Temkin equilibrium constant (L/g) corresponding to the maximum binding energy,

Dubinin-Radushkevich model is infrequently applied onto liquid phase adsorption due to its complex nature [37]. It accept heterogeneous surface with Gaussian energy distribution. It characterizes an imperative parameter to be specific mean free energy which is utilized to differentiate the physical and chemical adsorption. The equation is given in Table 1 where q_{mDR} (mg/g) is the capacity of saturation theory (mg/g), K_{DR} (mol^2/kJ) is the constant of adsorption energy and ε is the potential Polaniyi.

The equation defining the Elovich model is based on a kinetic principle assuming that the adsorption sites increase exponentially with adsorption which implies a multilayer adsorption [38]. It is expressed in Table 1

Table 1: Used isotherm models and their linear and non-linear forms.

	Non-Linear form	Linear form	Plot
Models with two-parameters			
Langmuir-1	$q_e = \frac{q_{mL}.K_L.C_e}{1+K_L.C_e}$	$\frac{C_e}{q_e} = \frac{1}{q_{mL}}C_e + \frac{1}{q_{mL}K_L}$	Ce/q_e vs C_e
Langmuir-2	-	$\frac{1}{q_e} = \frac{1}{q_{mL}K_L}\left(\frac{1}{C_e}\right) + \frac{1}{q_{mL}}$	$1/q_e$ vs $1/C_e$
Langmuir-3	-	$q_e = q_{mL} - \left(\frac{1}{K_L}\right)\frac{q_e}{C_e}$	q_e vs q_e/C_e
Langmuir-4	-	$\frac{q_e}{C_e} = K_L q_{mL} - K_L q_e$	q_e/C_e vs q_e
Freundlich	$q_e = K_F.C_e^{1/n}$	$\ln q_e = \ln K_F + \frac{1}{n}\ln C_e$	$\ln q_e$ vs $\ln C_e$
Temkin	$q_e = \frac{RT}{B_T}\ln K_T C_e$	$q_e = \frac{RT}{B_T}\ln K_T + \frac{RT}{B_T}\ln C_e$	q_e vs $\ln C_e$
Dubinin Radushkevich	$q_e = q_{mDR}e^{-K_{DR}\varepsilon^2}$ $\varepsilon = RT\ln\left(1+\frac{1}{C_e}\right)$	$\ln q_e = \ln q_{mDR} - K_{DR}\varepsilon^2$	$\ln q_e$ vs ε^2
Elovich	$\frac{q_e}{q_{mE}} = K_E C_e \exp\left(\frac{q_e}{q_{mE}}\right)$	$\ln\frac{q_e}{C_e} = \ln K_E q_{mE} - \frac{q_e}{q_{mE}}$	$\ln q_e/C_e$ vs qe
Models with three-parameters			
Langmuir-Freundlich	$q_e = \frac{q_{mLF}(K_{LF}C_e)^\beta}{1+(K_{LF}C_e)^\beta}$	$\frac{q_{mLF}}{q_e} = 1 + \frac{1}{(K_{LF}C_e)^\beta}$	q_{mLF}/q_e vs $1/C^\beta$
Redlich–Peterson	$q_e = \frac{A C_e}{1+B C_e^\beta}$	$\frac{C_e}{q_e} = \frac{1}{A} + \frac{B}{A}C_e^\beta$	C_e/q_e vs C_e^β
Sips	$q_e = \frac{q_{mS}K_s C_e^\beta}{1+K_s C_e^\beta}$	$\frac{q_{mS}}{q_e} = 1 + \frac{1}{K_s C_e^\beta}$	q_{mS}/q_e vs $1/C^\beta$
Fritz–Schlunder	$q_e = \frac{q_{mFS}K_{FS}C_e}{1+K_{FS}C_e^\alpha}$	$\frac{C_e}{q_e} = \frac{1}{K_s q_{mFS}} + \frac{1}{q_{mFS}}C_e^\alpha$	C_e/q_e vs C^α
Toth	$q_e = \frac{q_{mT}C_e}{(1/K_T + C_e^\alpha)^{1/\alpha}}$	$\left(\frac{C_e}{q_e}\right)^\alpha = \left(\frac{1}{K_T^{(\frac{1}{\alpha})}q_{mT}}\right)^\alpha + \left(\frac{1}{q_{mT}}\right)^\alpha C_e^\alpha$	$\left(\frac{C_e}{q_e}\right)^\alpha$ vs C_e^α
Models with four- parameters			
Fritz–Schlunder	$q_e = \frac{A C_e^\alpha}{1+B C_e^\beta}$	-	-
Baudu	$q_e = \frac{q_{m0}b_0 C_e^{(1+x+y)}}{1+b_0 C_e^{(1+x)}}$ $b = b_0 C_e^x$ $q_{mL} = q_{m0}C_e^y$	-	-
Model with five- parameters			
Fritz–Schlunder	$q_e = \frac{q_{mFS}K_{1FS}C_e^{m1}}{1+K_{2FS}C_e^{m2}}$	-	-

by where K_E is the Elovich equilibrium constant (L/mg) and q_{mE} is the Elovich maximum adsorption capacity (mg/g).

The parameters of Langmuir-Freundlich model are defined as follow: q_e is the adsorbed amount at equilibrium (mg/g), q_{mLF} is the Langmuir-Freundlich maximum adsorption capacity (mg/g), C_e is the adsorbate equilibrium concentration (mg/L), K_{LF} the equilibrium constant for a heterogeneous solid, and β is the heterogeneity parameter lies between 0 and 1.

The Redlich–Peterson [39] isotherm is an empirical isotherm incorporating three parameters. It combines elements from both the Langmuir and Freundlich equations and the mechanism of adsorption is a hybrid and does not follow ideal monolayer adsorption.

The parameters of this model are given in Table 1 where B is the Redlich–Peterson isotherm constant (L/g), A is also a constant having unit of (L/mg), and β is an exponent that lies between 0 and 1. C_e is the equilibrium liquid-phase concentration of the adsorbate (mg/L) and q_e is the equilibrium adsorbate loading onto the adsorbent (mg/g).

At high liquid-phase concentrations of the adsorbate, the Redlich–Peterson equation is reduced to the Freundlich equation where B /A and (1-β) present, respectively, the parameters K_F and 1/*n* of the Freundlich model. For β = 1, the Redlich–Peterson equation is reduced to the Langmuir equation, with b = A is the Langmuir adsorption constant (L/mg) related to the energy of adsorption and B = b q_{mL}, where q_{mL} signifies the Langmuir maximum adsorption capacity of the adsorbent (mg/g). For β = 0, the Redlich–Peterson equation is reduced to the Henry's equation, with B/(1 + A) is the Henry's constant.

Recognizing the problem of the continuing increase in the adsorbed amount with an increase in concentration in the Freundlich equation, Sips [40] proposed an equation similar in form to the Freundlich equation, but it has a finite limit when the concentration is sufficiently high. Table 1 shows the parameters of this equation where q_e is the adsorbed amount at equilibrium (mg/g), C_e the equilibrium concentration of the adsorbate (mg/L), q_{mS} the Sips maximum adsorption capacity (mg/g), K_S the Sips equilibrium constant (L/mg), and β is the Sips model exponent.

The *Fritz–Schlunder* [41] equation is represented in Table 1 where q_e is the adsorbed amount at equilibrium (mg/g), C_e the equilibrium concentration of the adsorbate (mg/L), q_{mFS} the Fritz–Schlunder maximum adsorption capacity (mg/g), K_{FS} the Fritz–Schlunder equilibrium constant (L/mg), and α is the Fritz–Schlunder model exponent.

Toth [42] has modified the Langmuir equation to reduce the error between experimental data and predicted values of equilibrium adsorption data. The application of his equation is best suited to multilayer adsorption similar to BET isotherms which is a special type of Langmuir isotherm and has very restrictive validity [43]. The Toth correlation is given in Table 2 where q_e is the adsorbed amount at equilibrium (mg/g), Ce the equilibrium concentration of the adsorbate (mg/L), q_{mT} the Toth maximum adsorption capacity (mg/g), K_T the Toth equilibrium constant, and α is the Toth model exponent.

Another four-parameter equation of Langmuir–Freundlich type was developed empirically by *Fritz* and *Schlunder* [41]. It is expressed in Table 1 with α and β ≤ 1 where q_e is the adsorbed amount at equilibrium (mg/g), C_e the equilibrium concentration of the adsorbate (mg/L), A and B are the Fritz–Schlunder parameters, and α and β are the Fritz–Schlunder equation exponents.

At high liquid-phase concentrations of the adsorbate, the Fritz and Schlunder equation is reduced to the Freundlich equation where A/B and (α-β) present the parameters K_F and 1/n of the Freundlich model respectively. For α = β = 1, The equation is reduced to the Langmuir equation with b = B is the Langmuir adsorption constant (L/mg) related to the energy of adsorption and A = b q_{mL}, where q_{mL} signifies the monolayer adsorption capacity of the adsorbent (mg/g).

Baudu [44] has remarked that the calculation of the Langmuir coefficients, b and q_{mL}, by the measurement of tangents at different equilibrium concentrations shows that they are not constants in a broad concentration range. So, he proposed a transformed Langmuir equation shown in Table 1 with (1 + *x* + *y*) and (1 + *x*) < 1. Graphical study of ln b = *f*(ln C_e) and ln $q_{m\,L}$ = *f* (ln C_e) gives access to b_o, q_{mo}, x, and y, where q_e is the adsorbed amount at equilibrium (mg/g), Ce the equilibrium concentration of the adsorbate (mg/L), q_{m0} the Baudu maximum adsorption capacity (mg/g), b_o the equilibrium constant, and *x* and *y* are the Baudu parameters.

Fritz and *Schlunder* [41] have proposed a five-parameters empirical expression which can represent

Table 2: Abbreviations and mathematical expression of used error functions.

Error function	Expression
Coefficient of determination R^2	$R^2 = \frac{\sum_{i=1}^{n}\left(q_{e,exp} - \overline{q_{e,cal}}\right)_i^2}{\sum_{i=1}^{n}\left(q_{e,exp} - q_{e,cal}\right)^2 + \left(q_{e,exp} - \overline{q_{e,cal}}\right)^2}$
Sum of squares errors SEE :	$SEE = \sum_{i=1}^{n}\left(q_{e,exp} - q_{e,cal}\right)_i^2$
Sum of absolute errors SAE :	$SAE = \sum_{i=1}^{n}\left\|q_{e,exp} - q_{e,cal}\right\|_i^2$
Average Relative Error ARE :	$ARE = \frac{100}{n}\sum_{i=1}^{n}\left\|\frac{q_{e,exp} - q_{e,cal}}{q_{e,exp}}\right\|_i^2$
Mean Square Error : MSE	$MSE = \frac{100}{n-2}\sum_{i=1}^{n}\left(q_{e,exp} - q_{e,cal}\right)_i^2$
Root Mean Square Error : RMSE	$RMSE = \sqrt{\frac{100}{n-2}\sum_{i=1}^{n}\left(q_{e,exp} - q_{e,cal}\right)_i^2}$

abroad field of equilibrium data (with m_1 and $m_2 \leq 1$) (Table 1). q_e is the adsorbed amount at equilibrium (mg/g), C_e the equilibrium concentration of the adsorbate (mg/L), q_{mFS} the Fritz-Schlunder maximum adsorption capacity (mg/g) and K_{1FS}, K_{2FS}, m_1, and m_2 are the Fritz–Schlunder parameters.

Error functions

Mathematically error functions such as coefficient of determination R^2, Sum of the Squared Errors (SSE), Sum of the Absolute Errors (SAE), the Average Relative Error (ARE), the Mean Square Error (MSE) and the Root Mean Square Error (RMSE) were employed. These functions were used to compare between the linear and non-linear regression methods and in order to find the best fit isotherm model to the experimental equilibrium data (using the solver add-in functions of Microsoft Excel software and Origin Pro 2017). The expression of the error functions are given in Table 2 where, $q_{e,cal}$ and $q_{e,exp}$ are respectively, the calculated and the experimental value of the equilibrium adsorbate concentration in the solid phase (mg/g) and n is the number of data points.

RESULTS AND DISCUSSION

XRD, FTIR and MEB characterization

The XRD results show that the illite with main characteristic 2θ peaks at 21°, 27.5°, 37° is the major phase (Fig.1a). Other phases are also identified and observed at 22°, 42.5°, 50.5°, 60° and 68.5° (Quartz) and at 45°, 55.5° (Kaolinite). A Calcite is also present at 29.5° but as minor phase with very low XRD peaks. The indexation of diffraction peaks was realized according to the JCPDS Cards [45]. The XRD pattern of the crude clay after chemical treatment by NaCl solution is illustrated in Fig.1b and the structure was remained nearly intact; and therefore, the chemical treatment does not influence its structure. We also noticed the disappearance of the peak of the calcite phase (29.5°) (Fig. 2c), due to the adsorption of Pb^{2+} ions whose presence on the adsorbent surface can displace or hide the (*h k l*) planes of the calcite.

The FT-IR analysis was conducted with treated clay and treated clay adsorbed by Pb^{2+} ions in order to identify functional groups of treated clay involved in the adsorption (Fig. 2). The broad band at 3613 cm^{-1} is due to OH of the interlayer water while the peak 1432 cm^{-1} is attributed to the stretching vibration of adsorbed water molecules. The bands at 780 and 689 cm^{-1} referred to Si–O and Si–O–Si, respectively, attest the presence of tetrahedral silica layers. For the treated clay adsorbing Pb^{2+} ions (Fig. 2b), we notice the intensity of the peak at 990 cm^{-1} increased after the adsorption process.

The SEM micrograph of treated clay is shown in Fig. 3. The clay shows an irregular morphology

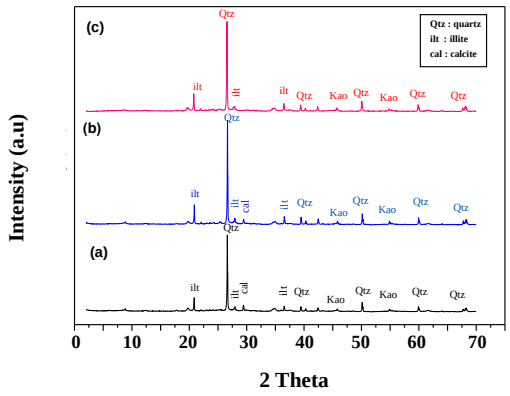


Fig. 1: XRD patterns of clay (a), activated clay (b) and clay after adsorption (c).

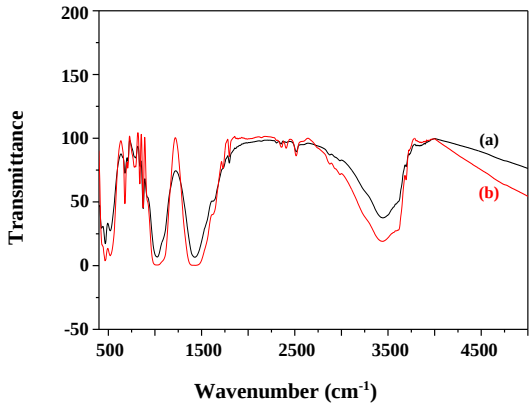


Fig. 2: FT-IR spectra of (a) treated clay after treated clay after Pb2+ ions adsorption.

of crystals. The results of the EDS analysis reveals the presence of different elements shown in Fig. 3.

The pH_{pzc} is one of the important parameters for discussion of pH effect. The pHpzc of treated clay was determined by the method cited in [34]. KNO_3 solution (0.01 M) was transferred to a series of Erlenmeyer flasks who are made up to exactly 100 mL. The initial pH of each flasks was adjusted by adding either HCl (0.1 M) or NaOH (0.1 M) to decrease or increase it respectively. 100 mg of treated clay was added to each flask. After stirring 48 h, the suspensions were filtered and the final pH values of the supernatant liquid (pH_{final}) were recorded. The pH_{ZPC} is the point where the curve pH final versus pH initial crosses the line the axis of the bisectors. pH_{ZPC} of treated clay was found to be at pH~ 8.53 (Fig. 4). At the solution pH ≤ 8.53, the active sites of the clay are protonated and have positive charge. However, at the pH values higher than the pH_{zpc}, the surface charge of the adsorbent is negative.

Effect of the experimental parameters on adsorption equilibrium

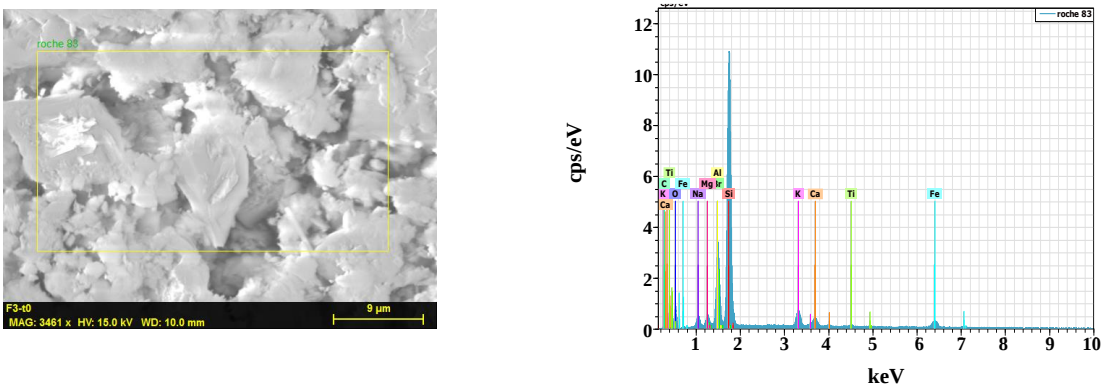
The effect of experimental parameters on the adsorption equilibrium as contact time, pH, initial Pb^{2+} ions concentration, adsorbent dosage and temperature were studies.

The effect of contact time on the removal of Pb^{2+} ions by treated clay at initial metal ion concentrations of 50 mg L^{-1} is shown in Fig. 5. The contact time was varied from 5 to 90 min at constant temperature of 25 °C. The time plot shows that the removal of adsorbate is rapid in early stages for the treated clay, but it gradually slows down until it reaches the equilibrium. This is due to the fact that a large number of vacant surface sites are available for adsorption during the initial stage, and after a lapse of time the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the solute molecules on the solid surface and in bulk phase [7, 25]. The contact time of 30 min was optimized and selected for the rest of the study.

The influence of pH on the adsorption of Pb^{2+} ions onto treated clay was investigated in the pH range of (1 –8). Fig. 6 shows the effect of pH on adsorption of Pb^{2+} ions onto treated clay. It can be observed from the results that the adsorption of Pb^{2+} ions increases with an increase in pH of the solution to a maximum around a pH ~7.0, and then decreases as the pH becomes more basic due to the precipitation of some Pb^{2+} ions.

At low pH, the number of H^+ ions increases, thus creating a bridge between the ligands between the treated clay and the Pb^{2+} ions, so that the surface of the adsorbents is closely associated with H^+ ions, which could hinder access of the metal ions, by repulsive forces, to the surface of the functional groups and consequently decrease the percentage of elimination of the metal. Therefore, the effect of a low pH on the sorption capacity can be interpreted as resulting from the competition of H^+ ions and metal ions for the binding sites [46-47]. Therefore, pH ~ 7 was selected for further studies.

The effect of initial Pb^{2+} ions concentrations on the adsorption performance of treated clay was investigated over a concentration range of 10 mg/L to 200 mg/L (Fig. 7). The adsorption capacity of the treated clay



Element	C	O	Na	Mg	Al	Si	K	Ca	Ti	Fe
Wt %	2.84	12.09	1.25	0.79	13.74	50.44	4.82	3.13	0.72	5.61

Fig. 3: SEM micrograph and EDS spectrum of treated clay.

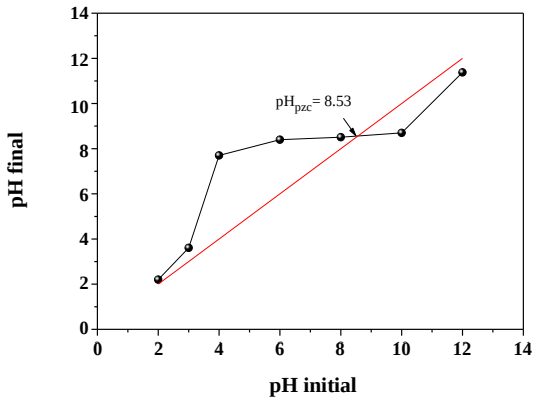


Fig. 4: Point of zero charge pH_{pzc} of the activated clay.

was found to increase with increase in initial lead ions. The results show that treated clay gave the maximum adsorption of 44 mg/g at 200 mg/L of initial Pb^{2+} ions concentration. The increase in adsorption with the increase in metal ion concentration is due to the driving force that initial concentration provides to overcome the mass transfer resistance between the aqueous and solid phases. The adsorption rate was high during the early adsorption period due to the availability of a large number of vacant sites, which increased the concentration gradient between the adsorbate in the solution and adsorbate on the adsorbent surface [1, 7, 23, 25]. The steady increase in the adsorption with the increase in initial metal ion concentration indicates that the adsorbents have very high potential for the removal of Pb^{2+} ions.

The results of the effect of adsorbent dosage on the adsorption efficiency of the treated clay are shown in Fig. 8 for Pb^{2+} ions removal. It was observed that the lead ion removal by the adsorbent increased as the adsorbent dosage increased gradually up to 2.5 g L^{-1} clay dosage. A further increase in dosage above 2.5 g L^{-1} gave no significant improvement in lead ion removal due to attainment of equilibrium between the adsorbent and adsorbate. This may be simply due to the increased availability of surface active sites resulting from the increased dose and conglomeration of the adsorbent the saturation is attributed to the occupation of active sites.

To examine the temperature effect on the Pb^{2+} ions retention, the conditions: initial Pb^{2+} ions concentration: 200 mg/L, agitation speed: 150 rpm, dose of adsorbent: 2 g/L; pH ~ 7 were kept while changing the temperature.

According to Fig. 9, when the temperature increases, the lead adsorption capacities decreases and the metal retention reaches its maximum at 25 °C; which would be due to an increase in desorption at high temperature confirming that adsorption is an exothermic phenomenon.

Comparisons of adsorption isotherm models

The comparison of isotherms results obtained using linear method is shown in Table 3. The error functions are used to select the optimum isotherm. The best-fit isotherm was selected based on the error functions that produced minimum error distribution between the experimental and calculated amount of lead adsorbed. Considering the values of error equations (SSE, MSE,

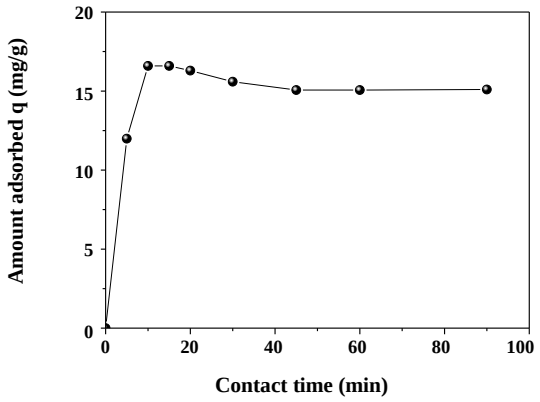


Fig. 5: Effect of contact time on amount of adsorption of Pb^{2+} ions by treated clay at initial concentration : 50 mg/L; pH ~ 7; agitation speed: 150 rpm; adsorbent dose: 2 g/L; temperature of solution: 25 °C.

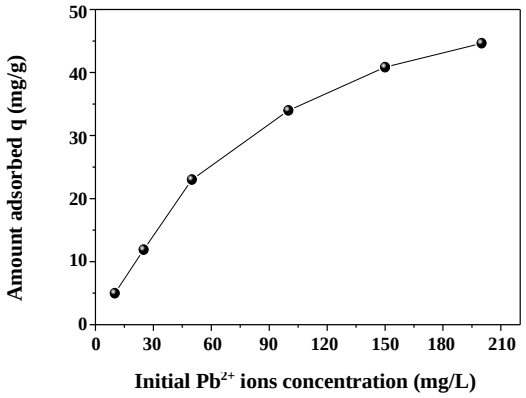


Fig. 7: Effect of initial Pb^{2+} ions concentration and adsorbent dosage on amount of adsorption of Pb^{2+} ions by treated clay (agitation speed: 150 rpm; pH: 7, temperature of solution: 25 °C).

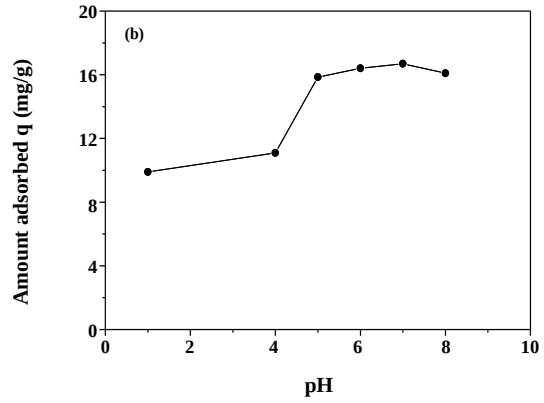


Fig. 6: Effect of pH on amount of adsorption of Pb^{2+} ions by treated clay at initial concentration : 50 mg/L; agitation speed: 150 rpm; adsorbent dose: 2 g/L; temperature of solution: 25 °C.

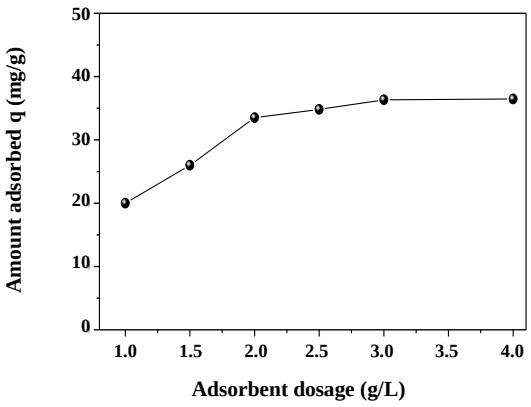


Fig. 8: Effect of adsorbent dosage on amount of adsorption of Pb^{2+} ions by treated clay (agitation speed: 150 rpm; pH: 7, temperature of solution: 25 °C).

SAE, ARE, RMSE and R^2), it was observed that the Freundlich isotherm model presents the lowest values of error, followed by Temkin isotherm, Langmuir, Elovitch, and Dubinin- Radushkevich isotherm respectively.

For non-linear method, a trial and error procedure, which is applicable to computer operation, was developed to determine the isotherm parameters by minimizing the error distribution between the experimental data and the isotherms studied. The calculated isotherm parameters and the corresponding error functions are given in Table 3. It seems that the error functions corresponding to the minimized deviations between the experimental equilibrium data and predicted isotherms suggested Freundlich and Langmuir as the best fit isotherms followed by Temkin, Dubinin-Radushkevich and Elovitch isotherm.

By comparing the error functions obtained by linear and non-linear regression method, it can be observed that the error functions of non-linear method are reduced. Except that of Temkin isotherm model, where the error functions are not changed for non-linear regression method. This could be explained by the great similitude between the linear and non-linear equation form for this model.

Analyzing the results given in Table 3 and the comparison of experimental and predicted adsorption isotherms of Pb^{2+} ions according to Freundlich, Langmuir and Temkin models (Fig. 10), it can be shown

Table 3: Linear and no-Linear isotherms models with two-parameters and error functions obtained for adsorption of Pb^{2+} ions onto treated clay.

Linear and isotherms models with two-parameters					
	Freundlich	Langmuir	Temkin	Dubinin-Radushkevich	Elovich
Parameters	K_F = 12.10 (mg/g)	q_{mL} = 45.04 (mg/g)	B_T = 454.55 (J/mol)	q_{mD} = 32.45 (mg/g)	q_{mE} = 8.08 (mg/g)
	n = 3.93	K_L = 0.23 (L/mg)	K_T = 20.33 (L/mg)	K_{D-R} = 2.82 10^{-4} (mol^2/kJ^2)	K_E = 10.84 (L/mg)
R^2	0.96948	0.95416	0.95755	0.7899	0.82996
SSE	40.31	61.54	56.77	344.9	263.5
MSE	10.07	15.38	9.46	86.22	65.88
SAE	11.41	16.36	15.66	38.07	33.59
ARE	7.839	22.49	23.65	27.89	33.32
RMSE	3.174	3.922	3.77	9.286	8.117
No-Linear and isotherms models with two-parameters					
	Freundlich	Langmuir	Temkin	Dubinin-Radushkevich	Elovich
Parameters	K_F = 3.89 (mg/g)	q_{mL} = 42.54 (mg/g)	B = 454.55 (J/mol)	q_{mD} = 39.57 (mg/g)	q_{mE} = 9.7 10^5 (mg/g)
	n = 1.967	K_L = 0.29 (L/mg)	K_T = 20.33 (L/mg)	K_{D-R} = 7.4 10^{-4} (mol^2/kJ^2)	K_E = 2.2.10^{-5} (L/mg)
R2	0.98256	0.9626	0.95755	0.88475	0.61634
SSE	22.72	49.89	56.77	167.9	1076.3
MSE	5.68	12.473	9.46	42	269
SAE	9.795	13.46	15.66	30.37	72.62
ARE	12.72	19.19	23.65	34.31	63.18
RMSE	2.38	3.53	3.77	6.48	16.4

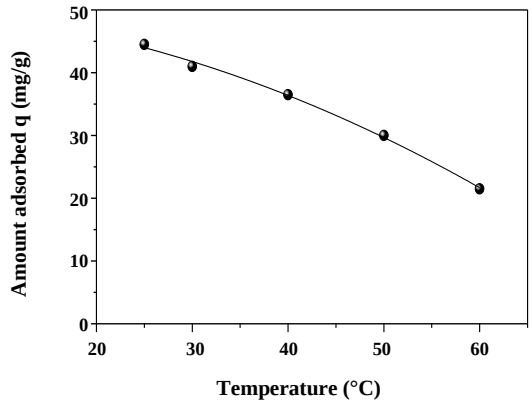


Fig. 9: Effect of temperature on amount of adsorption of Pb^{2+} ions by treated clay. (agitation speed: 150 rpm; initial concentration ion 200 mg/L; pH ~7 and adsorbent dose: 2 g/L).

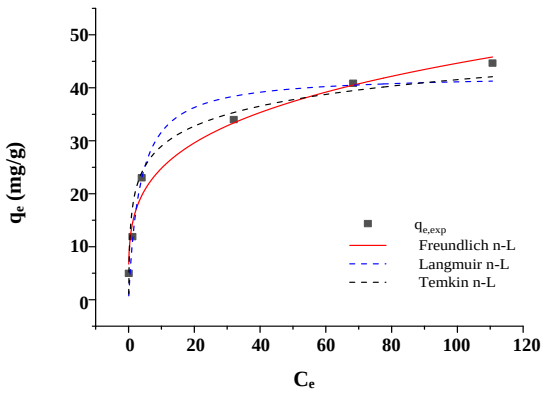


Fig. 10: Comparison of experimental and predicted adsorption isotherms of Pb^{2+} ions according to Freundlich, Langmuir and Temkin models (two-parameters).

Table 4: Comparison of linear and non-linear isotherms models with three parameters and error functions obtained for adsorption of Pb^{2+} ions onto treated clay.

Isotherm Models	Unknown Parameters			Error Functions					
				SSE	MSE	SAE	ARE	RMSE	R^2
Langmuir-Freundlich	q_{mLF}	K_{LF}	β						
Linear	69.68	0.03	0.42	11.89	3.96	6.58	6.88	1.99	0.99080
Non-linear	69.68	0.03	0.42	11.89	3.96	6.58	6.88	1.99	0.99080
Sips	q_{ms}	K_s	β						
Linear	69.6	0.23	0.42	11.89	3.96	6.58	6.88	1.99	0.99080
Non-linear	69.6	0.23	0.42	11.89	3.96	6.58	6.88	1.99	0.99080
Fritz- Schluender	q_{mFS}	K_{FS}	α						
Linear	14.25	47.7	0.75	19.40	1697	154	97.65	41.2	0.98508
Non-linear	15.88	7.31	0.77	15.47	5.16	7.29	9.93	2.27	0.98806
Redlich-Peterson	β	B	A						
Linear	0.77	7.28	115.6	15.47	5.16	7.29	9.95	2.27	0.98806
Non-linear	0.77	7.28	115.6	15.47	5.16	7.29	9.95	2.27	0.98806
Tôth	q_{mT}	K_T	α						
Linear	747.2	0.29	0.28	1051	350.6	67.68	46.62	18.73	0.61036
Non-linear	123.3	1.88	0.19	11.94	3.98	6.56	8.05	2.00	0.99076

that the model of Freundlich is the best to represent the experimental data of Pb^{2+} ions adsorption onto treated clay. Indeed, this model gives a relatively high error values R^2 and the lowest other error values.

The abilities of the three parameters equations, Langmuir–Freundlich, Redlich–Peterson, Sips, Fritz–Schlunder, and Toth isotherms to model the equilibrium adsorption data were examined. Table 4 shows the isotherms parameters obtained using the linear and non-linear fitting analysis. The better and perfect representation of the experimental results of the adsorption isotherms is obtained using the Langmuir–Freundlich and sips model. According to Table 4, the coefficients of determination are very good ($R^2 \geq 0.990$).

Langmuir-Freundlich model constants namely q_{mLF}, K_{LF} and β were calculated using curve fitting tool (OriginPro 2017) and given in the Table 4. R^2 values for Langmuir-Freundlich model were 0.9908 for non-linear and linear case. This model has shown high R^2 values and low values for SSE, MSE, SAE, ARE and RMSE (for both linear and non-linear models) among all other three parameters models except sips model. The value of the maximum adsorption capacity obtained using the Langmuir-Freundlich equation are higher than those calculated by the Langmuir, Freundlich, and the theoretical values.

The prediction of adsorption isotherms of lead onto treated clay by the Sips model is shown in Fig.11. The Sips equation fits adequately the experimental results. On the basis of the error functions values (Table 4). The maximum adsorption capacities are identical to those obtained using the Langmuir–Freundlich isotherm. The parameter K_S and mS change in the same manner as the constants K_{LF} and m_{LF} of the equation of Langmuir–Freundlich.

The non-linear regression of Fritz- Schluender model gave parameters values like the Redlich-Peterson model affirming the theoretical correspondence of these two models as shown in the Table 4. The parameters got as a result of the linear regression and coefficient of determination as well as other functions given in Table 4 does not fulfill the experimental data.

Linear and non-linear trends of Toth model are shown in Table 4 which depicts a poor fit for linear model and

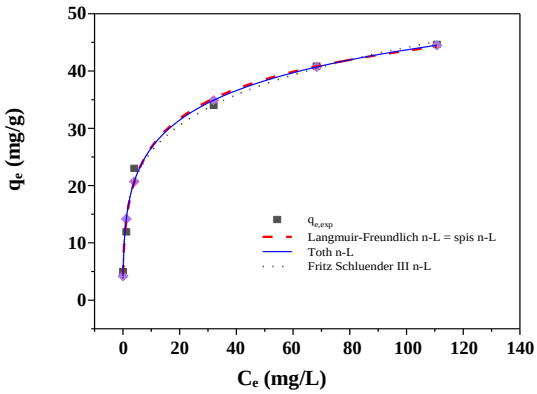


Fig. 11*: *Comparison of experimental and predicted adsorption isotherms of Pb^{2+} ions according to Langmuir-Freundlich, Sips, Toth and Fritz-Schluender models (three parameters).

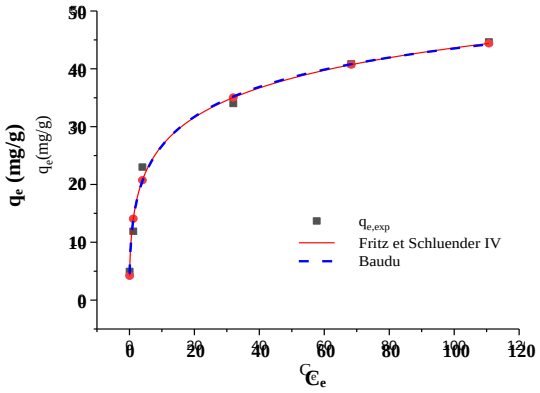


Fig. 12*: *Comparison of experimental and predicted adsorption isotherms of Pb^{2+} ions according to Fritz-Schluender and Baudu models (Four and Five-parameters).

a fine correlation in case of non-linear model. This is stated by comparing the values of R^2 and other error functions given in Table 4. When mT is less than 1, it suggests that adsorption occurs on a heterogeneous surface. For homogeneous adsorbents mT is equal to 1. The Toth model exponent mT assessed by linear and non-linear regression lies between 0 and 1 recommending a decent correspondence of Toth isotherm with Langmuir isotherm as shown in Table 4.

The results obtained using the three-parameter equations show that the best-fitted adsorption isotherm models were determined to be in the order: Langmuir–Freundlich = Sips > Toth > Redlich-Peterson = Fritz-Schluender. The above order revealed that the equilibrium data are better fitted by the three-parameter models rather than the two-parameter models. The Langmuir–Freundlich model was found to best represent the equilibrium data.

The adsorption data were analyzed according to the non-linear form of the four-parameters isotherm models. An appropriate fitting of the experimental results of adsorption isotherms is obtained using the four-parameter model of Fritz–Schlunder (Fig. 12). From Table 5, the coefficients of determination (≥0.9908) are very good and low values for SSE, MSE, SAE, ARE and RMSE

The prediction of equilibrium adsorption isotherms of lead by the Baudu model is presented on Fig. 12. An excellent description of the experimental results is obtained using the model of Baudu. On the basis of the average percentage error values (Table 5). The equation of Fritz-Schlunder seems better than that of Baudu. The value of the maximum adsorption capacity obtained using the Baudu isotherm are higher than those calculated by the Langmuir, Freundlich models and also superior to the theoretical values.

The adsorption data were analyzed according to the non-linear form of the five-parameters isotherm model of Fritz-Schlunder. An adequate fitting of the experimental results of the adsorption isotherms is obtained using the five-parameters model of Fritz-Schlunder. From Table 5, the coefficients of correlation are very good (≥ 0.99107) and low values for SSE, MSE, SAE, ARE and RMSE.

The value of the maximum adsorption capacity obtained using the Fritz-Schlunder (five-parameters) are better than that of Langmuir-Freundlich and Sips (three-parameters). The five-parameter models of Fritz-Schlunder are better than that of Baudu and Fritz-Schlunder with three-parameters.

Kinetic Study

The pseudo first order kinetic model is given by the accompanying differential equation [12, 37].

$$\frac{dq_t}{dt} = K_t\left(q_e - q_t\right) \qquad (2)$$

Where, q_t and q_e are instantaneous and equilibrium uptakes (mg g^{-1}) respectively. k_1 (min^{-1}) is the pseudo first order rate constant. Eq. (3) results in the accompanying linearized form for the conditions of $q_t = 0$ at $t = 0$. Linear plots ln ($q_e - q_t$) vs. t (Fig. 13) indicate the graphical conduct of pseudo first order kinetic model.

$$\ln\left(q_e - q_t\right) = \ln q_e - K_1 \cdot t \qquad (3)$$

Table 5: Comparison of linear and non-linear isotherms models with Four and Five-parameters and error functions obtained for adsorption of Pb^{2+} ions onto treated clay.

	Fritz et Schluender IV (four-parameters)		Baudu (four parameters)		Fritz et Schluender V (five-parameters)	
Parameters	A	21.21	q_{m0}	75.07	qm	46.85
	B	0.59	b_0	0.21	K_1	0.71
	α	0.51	*x*	-0.56	K_2	1.62
	β	0.42	*y*	-0.01	α	0.096
					β	-0.42
	R^2	0.9911	R^2	0.9908	R^2	0.9911
Error Functions	SSE	11.5	SSE	11.54	SSE	11.5
	MSE	1.9	MSE	1.92	MSE	1.92
	SAE	6.6	SAE	6.62	SAE	4.61
	RMSE	7.9	RMSE	7.93	RMSE	7.9
	ARE	1.7	ARE	1.7	ARE	1.7

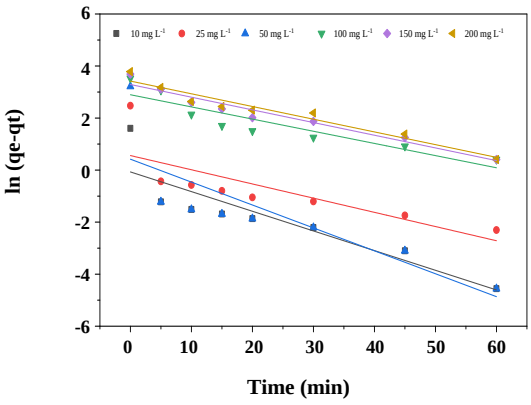


***Fig. 13*: Pseudo-first order kinetic plots for the adsorption of Pb^{2+} ions onto treated clay at different concentrations.**

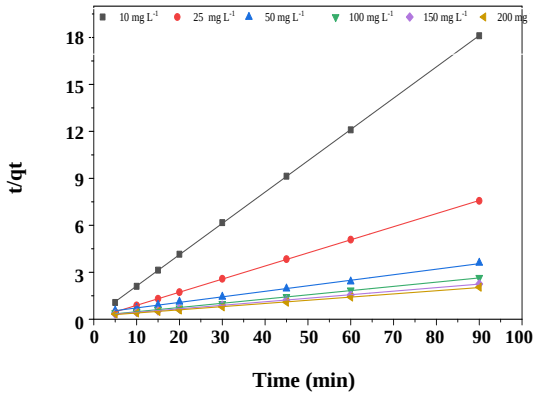


***Fig. 14*: Pseudo-second-order kinetic plots for the adsorption of Pb^{2+} ions onto treated clay at different concentrations.**

The non-linear type of the pseudo first order kinetic model is given as follows:

$$q_t = q_e\left(1 - e^{-K_1 t}\right) \tag{4}$$

The pseudo second order kinetics can be determined using following rate equation [12, 37].

$$\frac{dq_t}{dt} = K_2\left(q_e - q_t\right)^2 \tag{5}$$

Where, K_2 (g/mg.min) is pseudo second order rate constant. Eq. (6) gives a linear equation on integration with initial conditions of at t = 0 and q_t = 0.

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \tag{6}$$

The term $K_2q_e^2$ is termed as initial sorption rate represented by *h* (mg/g.min) and non-linear form is as follows:

$$q_t = \frac{q_e^2 K_2 t}{1 + q_e K_2 t} \tag{7}$$

A linear plot of t/q_t vs t demonstrates the graphical conduct of pseudo second order kinetic model (Fig.14).

Linear regression is frequently used to determine the best fitting kinetic model; the best-fit kinetic equation

Table 6: Kinetic data obtained by linear regression of two used kinetic models.

	Pseudo-First-Order (linear regression)					Pseudo-Second-Order (linear regression)			
Concentration (mg L^{-1})	$q_{e,,exp}$ (mg g^{-1})	$q_{e,cal}$ (mg g^{-1})	K_1 (min^{-1})	R^2	SSE	$q_{e,,cal}$ (mg g^{-1})	K_2 (g mg^{-1} min^{-1})	R^2	SSE
10	04.97	0.922	0.075	0.7978	0.45	5.003	0.3236	0.9996	0.0833
25	11.90	1.748	0.054	0.6273	0.94	11.95	0.1319	0.9994	0.2357
50	23.00	20.31	0.051	0.9903	11.01	28.33	0.0034	0.9983	0.3812
100	34.00	22.91	0.050	0.9245	12.5	37.04	0.0035	0.9982	1.0993
150	40.85	31.32	0.051	0.9860	17.01	44.25	0.0024	0.9984	0.3523
200	44.65	35.48	0.056	0.9843	18.73	49.26	0.0021	0.9988	0.8137

Table 7: Kinetic data obtained by non-linear regression of two used kinetic models.

		Pseudo-First-Order (non-linear regression)				Pseudo-Second-Order (non-linear regression)			
Concentration (mg L^{-1})	$q_{e,,exp}$ (mg g^{-1})	$q_{e,cal}$ (mg g^{-1})	K_1 (min^{-1})	R^2	SSE	$q_{e,,cal}$ (mg g^{-1})	K_2 (g mg^{-1} min^{-1})	R^2	SSE
10	04.97	4.75	0.62	0.9979	0.09	5.65	0.0173	0.9971	0.62
25	11.90	11.5	0.65	0.9980	0.76	13.54	0.0073	0.9971	0.70
50	23.00	24	0.07	0.9888	0.93	28.55	0.0032	0.9976	0.39
100	34.00	32	0.09	0.9973	0.97	37.86	0.0031	0.9913	1.03
150	40.85	38	0.08	0.9903	1.37	44.36	0.0023	0.9992	0.33
200	44.65	42	0.078	0.9972	2.19	50.08	0.0019	0.9971	0.77

is selected based on the error functions that produced minimum error distribution between the predicted and experimental values. The Slopes and intercepts of plots of the linear representations (Fig. 13 and Fig. 14) were obtained to determine the rate constants and equilibrium adsorption amount q_e of the pseudo-first order and pseudo-second order. Table 6 shows the calculated K_1 and qe values and the corresponding error function values.

From Table 6, it was observed that the R^2 values were high for the pseudo-second order ($\geq$ 0,99) but were low for the pseudo-first order model. The SSE values confirms the good fit of the experimental data with the pseudo-second order model more than with the pseudo-first order. In consequence, by using the linear regression method the pseudo-second order model was found to well define the kinetic of adsorption of lead into the treated clay.

In the case of the non-linear method, the software Origin lab version 9 was used for determining the pseudo-first-order and pseudo-second-order kinetic parameters. The kinetic parameters determined by the non-linear method are listed in Table 7. From these results, it was observed that the nonlinear forms (pseudo-first-order, pseudo-second-order) exhibited higher R^2 values than the linear forms. Furthermore, the error function (SSE) exhibited a lower value than those of the linear forms for the whole range of experimental data.

From Table 7, it was observed that the kinetic parameters associated with the pseudo-second-order model calculated by linear and nonlinear methods varied a little. However, when the values of the error function (SSE) corresponding to the non-linear pseudo-second-order equation were analyzed, it was observed that the values of the error function were lower than those of the linear form. Therefore, the non-linear pseudo-second-order kinetic model was better than the pseudo-first-order model in the simulation of kinetics of lead onto the treated clay.

Comparison of Algerian treated clay with various adsorbents

The comparison of adsorption capacity of the Algerian treated clay with that of various adsorbents is given in Table 8. The Algerian treated clay has a high adsorption capacity as comparable with that of the other adsorbents.

Table 8: Comparison of maximum adsorption capacities of Pb2+ ions by various adsorbents.

Adsorbent	Adsorption capacity, qm (mg/g)	References
Jordanian Kaolinite	13.32	[48]
Polyphosphate-modified kaolinite Clay	25.13	[49]
Clinoptilolite	27.70	[50]
Montmorillonite	31.10	[51]
PVA-modified Kaolinite clay	36.23	[52]
Tetraborate modified Kaolinite clay	42.92	[53]
Algerian treated clay	46.85	This work
Smectite	49.56	[54]

CONCLUSIONS

The ability of treated clay to remove Pb^{2+} ions from aqueous solutions has been studied at different operating conditions: contact time, initial metal ion concentrations, dose of adsorbent, pH, and temperature. The optimum pH for lead ions retention was found 7.0 for the treated clay. The effect of temperature on the adsorption phenomenon was also investigated. The results indicated that adsorption is an exothermic process for lead ions removal

The results of the present study show that the non-linear regression method was the best method to obtain the isotherm parameters and to select the optimum isotherm, compared to that of the linear regression. The comparison between non-linear isotherms shows that the Fritz-Schlünder isotherm is the best-fitting model for the adsorption of lead onto treated clay.

The classification of all the tested models for the description of adsorption equilibrium isotherms of lead on treated clay is as follows: Fritz–Schlunder (five-parameters) > Langmuir–Freundlich (three- parameters) = Sips > Toth > Fritz–Schlunder (four-parameters) > Baudu > Redlich–Peterson > Fritz–Schlunder(three-parameters) > Freundlich > Langmuir > Temkin > Dubinin-Radushkevich > Elovich.

This study shows that the best-fitting non-linear forms of the pseudo-first-order and pseudo-second-order kinetic models were superior to the linear forms. The model parameters may be distorted when the non-linear equations were transformed to linear forms Moreover, the non-linear kinetic equations have the advantage of there being no need to know the value of $q_{e,exp}$ before fitting the experimental points. Therefore, the non-linear method should be primarily adopted to obtain adsorption parameters. In addition, the error analysis using the SSE method may be better than using the determination coefficient (R^2) to determine the best-fitting models.

Received : Jan. 14, 2019 ; Accepted :Apr. 21, 2019

REFERENCES

[1] Mekatel H., Amokrane S., Benturki A., Nibou D., Treatment of Polluted Aqueous Solutions by Ni^{2+}, Pb^{2+}, Zn^{2+}, Cr^{+6}, Cd^{2+} and Co^{2+} Ions by Ion Exchange Process Using Faujasite Zeolite, *Proc. Eng.*, **33**: 52–57 (2012).

[2] Nibou D., Amokrane S., Catalytic Performances of Exchanged Y Faujasites by Ce^{3+}, La^{3+}, UO_2^{2+}, Co^{2+}, Sr^{2+}, Pb^{2+}, Tl^{+} and NH_4^{+} Cations in Toluene Dismutation Reaction, *Compt. Rend. Chim.*, **13**(5): 527-537 (2010).

[3] Spiro G.T., Stigliani W.M., "Chemistry of the Environment", Prentice-Hall, New Jersey (1996).

[4] Sitting M., "Handbook of Toxic and Hazardous Chemicals", Noyes Publications, Park Ridge, NJ, (1981).

[5] Zehhaf A., Benyoucef A., Berenguer R., Quijada C., Taleb S., Morallon, E., Lead Ion Adsorption from Aqueous Solutions in Modified Algerian Montmorillonites, *J. Therm. Anal. Calorim.*, **110**(3): 1069-1077 (2011).

[6] Patterson J.W., "Industrial Wastewater Treatment Technology", 2nd Ed., Butterworth–Heinemann, London *(*1985).

[7] Nibou D., Lebaili S., Determination of Exchange Rate of Lead and Uranium in NaY and NaZSM-5 by Inductively Coupled Plasma Atomic Emission Spectroscopy and Polarography, *Quim. Anal.*, **16**: 147-152 (1997).

[8] Goleij, M., Fakhraee, H. Response Surface Methodology Optimization of Cobalt (II) and Lead (II) Removal from Aqueous Solution using MWCNT-Fe_3O_4 Nanocomposite, *Iran. J. Chem. Chem. Eng. (IJCCE)*, **36**(5), 129-141 (2017).

[9] Poorsadeghi, S., Kassaee, M. Z., Fakhri, H., Mirabedini, M., Removal of Arsenic from Water Using Aluminum Nanoparticles Synthesized Through Aec Discharge Method, *Iran. J. Chem. Chem. Eng. (IJCCE)*, **36(4)**: 91-99 (2017).

[10] Houhoune F., Nibou D., Chegrouche S., Menacer S., Behaviour of Modified Hexadecyltrimethylammonium Bromide Bromide Towar Uranium Species, *J. Env. Chem. Eng.* **4 (3)**: 3459-3467 (2016).

[11] Naseem R., Tahir S.S., Removal of Pb(II) from Aqueous/acidic Solutions by Using Bentonite as an Adsorbent, *Water Res.* **35**: 3982–3986 (2001).

[12] Mekatel H., Amokrane S., Bellal B., Trari M., Nibou D., Photocatalytic Reduction of Cr (VI) on Nanosized Fe_2O_3 Supported on Natural Algerian Clay: Characteristics, Kinetic and Thermodynamic Study, *Chem. Eng. J.*, **200:** 611-618 (2012).

[13] Barkat M., Chegrouche S., Mellah A., Bensmain B., Nibou D., Boufatit M., Application of Algerian Bentonite in the Removal of Cadmium (II) and Chromium (VI) from Aqueous Solutions, *J. Surf. Eng. Mater. Adv. Tech.* **4** (**04**): 210 (2014).

[14] Mekhloufi M., Zehhaf A., Benyoucef A., Quijada C., Morallon E., Removal of 8-Quinolinecarboxylic Acid Pesticide from Aqueous Solution by Adsorption on Activated Montmorillonite, *Environ. Monitor. Asses.*, **185**(12): 10365-10375 (2013).

[15] Zehhaf, A., Benyoucef, A., Quijada, C., Taleb, S., Morallon, E., Algerian Natural Montmorillonites for Arsenic(III) Removal in Aqueous Solution, *Inter. J. Env. Sci. Tech.*, **12(2)**: 595-602 (2015).

[16] Özcan A., Ömeroğlu Ç., Erdoğan Y., Özcan A. S., Modification of Bentonite with a Cationic Surfactant: An Adsorption Study of Textile dye Reaction Blue 19, *J. Hazard Mat.* **140 (1)**: 173–179 (2007).

[17] España V.A.A., Sarkar B., Biswas B., Rusmin R., Naidu R., Environmental Applications of Thermally Modified and Acid Activated Clay Minerals: Current Status of the Art., *Env. Techn. Innov.* (2016). DOI: http://dx.doi.org/10.1016/j.eti.2016.11.005.

[18] Belbachir I., Makhoukhi B., Adsorption of Bezathren Dyes Onto Sodic Bentonie from Aqueous Solutions., *J. Taiwan Inst. Chem. Eng.*, **75**. 105–111 (2017).

[19] Zivica V., Palou M.T., Physico-Chemical Characterization of Thermal Treated Bentonite, *Compos Part B-Eng.*, **68:** 436–445 (2015).

[20] Makhoukhi B., Didi M.A., Moulessehoul H., Azzouz A., Telon Dye Removal from Cu(II)-Containing Aqueous Media Using p-Diphosphonium Organomontmorillonite, *Me diter. J. Chem.*, **1**(2): 44–55 (2011).

[21] Mekatel H., Amokrane S., Bellal B., Trari M., Nibou D., Photocatalytic Reduction of Cr (VI) on Nanosized Fe_2O_3 Supported on Natural Algerian Clay: Characteristics, Kinetic and Thermodynamic Study, *Chem. Eng. J.*, **200:** 611-618 (2012).

[22] Meshram S., Limaye R., Ghodke S., Nigam S., Sonawane S., Chikate R., Continuous flow Photocatalytic Reactor Using ZnO–bentonite Nanocoposite for Degradation of Phenol,. *Chem. Eng.J.* **172**(2): 1008–1015 (2011).

[23] Krobba, A., Nibou, D., Amokrane, S., Mekatel, H., Adsorption of Copper (II) onto Molecular Sieves NaY, *Desal. Wat. Treat.*, **37**: 1–7 (2012).

[24] Aid A., Amokrane S., Nibou D., Mekatel E., Trari M., Hulea V., Modeling Biosorption of Cr (VI) onto Ulva Compressa L. from Aqueous Solutions, *Wat. Sci. Tech.*, **77** (**1**): 60-69 (2018).

[25] Blanchard G., Maunaye M., Martin G., Removal of Heavy Metals from Waters by Means of Natural Zeolites, *Water. Res*, **18**: 1501-1507 (1984).

[26] Amrhar O., Nassali H., Elyoubi M.S., Application of Nonlinear Regression Analysis to Select the Optimum Absorption Isotherm for Methylene Blue Odsorption onto Naturel Illitic Clay, *Bul. Soc. Roy. Sci. Liege* **84**: 116-130 (2015).

[27] Peric J., Trgo M., Vukojevic Medvidovic N., Removal of Zinc, Copper and Lead by Natural Zeolite-a Comparison of Adsorption Isotherme, *Wat. Resear.*, **38**: 1893-1899 (2004).

[28] Karadag D., Koc Y., Turan M., Ozturk M., A Comparative Study of Linear and Non-Linear Regression Analysis for Ammonium Exchange by Clinoptilinite Zeolite, *J. Hazrd. Mater.*, **144**: 432-437 (2007).

[29] Deepatana A., Valix M., Comparative Adsorption Isotherms and Modeling of Niclitekel and Cobalt Citrate Complexes onto Chelating Resins, *Desalination*, **218**: 334-342 (2008).

[30] Chowdhury, S., Misra, R., Kushwaha, P., Das, P., Optimum Sorption Isotherm by Linear and Nonlinear Methods for Safarin onto Alkali-Treated Rice Husk , *Bioremed. J.*, **15**(2): 77-89 (2011).

[31] Boldizsar N., Carmen M., Andrada M., Cerasella I., Barbu-Tudoran L., Cornelia M., Linear and Nonlinear Regression Analysis for Heavy Metals Removal Using Agaricus Bisporus Macrofungus, *Arab. J. Chem*., **10:** S3569-S3579 (2017).

[32] Gunay A., Application of Nonlinear Regression Analysis for Ammonium Exchange by Natural (Bigadic) Clinoptilolite, *J. Hazrd Mater.*, **148**: 708-713 (2007).

[33] Lamgmuir I., The Constitution and Fundamental Properties of Solids and Liquids, Part 1. Solids, *J. Am. Chem. Soc* **38**: 2221-2295 (1916).

[34] Boudechiche N., Yazid H., Trari M., Sadaoui, Z, Valorization of Crataegus Azarolus Stones for the Removal of Textile Anionic Dye by Central Composite Rotatable Design Using Cubic Model: Optimization, Isotherm and Kinetic Stydies, *Envir. Sci. Pol. Res.*, **24**(24): 19609-19623 (2017).

[35] Freundlich H., Über Die Adsorption in Losungen (Adsorption in Solution), *Zeitsch. Phys. Chem.*, **57**: 385–470 (1906).

[36] Temkin M.I., Adsorption Equilibrium and the Kinetics of Processes on Nonhomogeneous Surfaces and in the Interaction between Adsorbed Molecules, *Zh. Fiz. Chim*, **15**: 296-332 (1941).

[37] Nibou D., Khemaissia S., Amokrane S., Barkat M., Chegrouche S., Mellah A., **R**emoval of UO_2^{2+} onto Synthetic NaA Zeolite. Characterization, Equilibrium and Kinetic Studies, *Chem. Eng. J.*, **172**(1): 296-305 (2011).

[38] Elovich S.Y., Larinov O.G., Theory of Adsorption from Solutions of Non Electrolytes on Solid (I) Equation Adsorption from Solutions and the Analysis of Its Simplest form, (II) Verification of the Equation of Adsorption Isotherm from Solutions, *Izv. Akad. Nauk. SSSR, Otd. Khim. Nauk.*, **2**: 209–216 (1962).

[39] Redlich O., Peterson D.L., A Useful Adsorption Isotherm, *J. Phys. Chem.* **63**: 1024–1026(1959).

[40] Sips R., On the Structure of a Catalyst Surface, *J. Chem. Phys.* **16**: 490–495 (1948).

[41] Fritz W., Schlunder E.U., Simultaneous Adsorption Equilibria of Organic Solutes in Dilute Aqueous Solutions on Activated Carbon, *Chem. Eng. Sci.*, **29**: 1279–1282 (1974).

[42] Toth J., Calculation of the BET-Compatible Surface Area from Any Type I Isotherms Measured Above the Critical Temperature, *J. Colloid Interf. Sci,*. **225**: 378–383(2000).

[43] Amokrane S., Rebiai R., Nibou D., Behaviour of Zeolite A, Faujasites X and Y Molecular Sieves in Nitrogen Gas Adsorption, *J. Appl. Sci.*, **7**: 1985-1988 (2007).

[44] Baudu M., "Study of Interactions Solute-Fibres of Active Carbon. Application and Regeneration", Ph.D. Thesis, University of Rennes I, France (1990).

[45] Bergaya F., Theng B.K.G., Lagaly G., General Introduction Clays, Clay Minerals and Clay Science, Handbook of Clay Science : *Develop. Clay Sci*., **1:** 1-18 (2006).

[46] Low K.S., Lee C.K., Kek K.L., Removal of Chromium VI from Aqueous Solution, *Bio. Techn.*, **54**: 133-139 (1995).

[47] Onwu F.K., Ogah S.P.I., Studies on the Effect of pH on the Sorption of Cadmium (II), Nickel (II), Lead (II), and Chromium (VI) from Aqueous solutions by African White star Apple (Chrysophyllum albidium) Shell, *African J. Biotech.* **9**: 7086-7093 (2010).

[48] Al-Harahsheh M., Shawabkeh R., Al-Harahsheh A., Tarawneh K., Batiha M.M., Surface Modification and Characterization of Jordanian Kaolinite: Application for Lead Removal from Aqueous Solutions, *Appl. Surf. Sci.* **255:** 8098–8103 (2009).

[49] Amer M.W., Khalili F.I., Awwad A.M., Adsorption of Lead, Zinc and Cadmium Ions on Polyphosphate-Modified Kaolinite Clay, *J. Environ. Chem. Ecotoxicol*. **2:** 1–8 (2010).

[50] Sprynskyy M., Buszewski B., Terzyk A.P., Namiesnik J., Study of the Selection Mechanism of Heavy Metal (Pb^{2+}, Cu^{2+}, Ni^{2+}, and Cd^{2+}) Adsorption on Clinoptilolite, *J. Colloid Interface Sci.* **304**: 21–28 (2006).

[51] Gupta S.S., Bhattacharyya K.G., Immobilization of Pb(II), Cd(II) and Ni(II) Ions on Kaolinite and Montmorillonite Surfaces from Aqueous Medium, *J. Environ. Manage.* **87**: 46–58. (2008)

[52] Unuabonah E.I., Adebowale K.O., Olu-Owolabi B.I., Yang L.Z., Comparison of Sorption of Pb^{2+} and Cd^{2+} on Kaolinite Clay and Polyvinyl Alcohol-Modified Kaolinite Clay, *Adsorption* **14**: 791–803 (2008).

[53] Unuabonah E.I., Adebowale K.O., Olu-Owolabi B.I., Yang L.Z., Kong L.X., Adsorption of Pb (II) and Cd (II) from Aqueous Solutions onto Sodium Tetraborate-Modified Kaolinite Clay: Equilibrium and Thermodynamic Studies, *Hydrometallurgy*, **93**: 1–9 (2008).

[54] Jitniyom K., Suddhiprakarn A., Kheoruenromne I., "Adsorption of Lead, Zinc, Copper and Cadmium of Smectite", *Proceedings of the 50th Kasetsart University Annual Conference*, **Vol. 2**, Kasetsart University, Thailand, pp. 136–143 (2012)

Supplementary information

Table S1: Observed data of the adsorption experiments in order to assure the linear and non-linear regression calculations.

C_o(mg L^{-1})	Ce(mg L^{-1})	V(l)	m(g)	%	Q
10	0,06	0,1	0,2	99,4	4,970
25	1,2	0,1	0,2	95,2	11,900
50	4	0,1	0,2	92	23,000
100	32	0,1	0,2	68	34,000
150	68,3	0,1	0,2	54,467	40,850
200	110,7	0,1	0,2	44,65	44,650

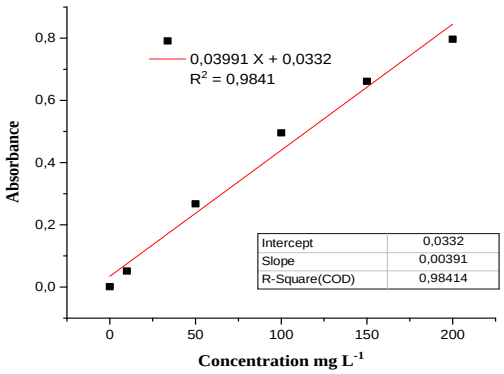


Fig. S1: Calibration curve of ranging from 0 to 200 mg L^{-1} of determination of Pb^{2+} concentration by a flame atomic absorption spectrophotometer