

## Optimization of experimental parameters for retention of Pb(II) ions from aqueous solution on clay adsorbent

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**Abstract.** The removal of Pb(II) ions is an important issue for the treatment of industrial wastewater, due to its serious consequences on environment and human health. In this study a local clay material was tested as adsorbent for the retention of Pb(II) ions from aqueous solution. The proposed method can be considered low-cost, mainly due to the high availability of clay material in this region, and the high removal percent of Pb(II) ions (> 99%) allows us to say that this method has a high efficiency. Therefore, the finding of the optimal values of the most important experimental parameters which affects the efficiency of Pb(II) ions adsorption on clay adsorbent, represent the next important step in highlighting the practical applicability of this process. The most important experimental parameters, including initial solution pH, adsorbent dose, initial Pb(II) ions concentration, contact time and temperature, were analyzed in batch systems. The obtained experimental results indicates that the efficiency of adsorption process is highest at initial solution pH of 7.0, 4.0 g adsorbent/L, 5 min of contact time and high temperature (50 °C). Under these conditions, the removal percent of Pb(II) ions is over 99 % over the initial concentration range between 20 and 310 mg Pb(II)/L. The results of this study suggest that this clay material is an excellent adsorbent for Pb(II) ions removal and broadens the potential applicability of these materials in environmental remediation.

### 1. Introduction

As a result of technological progress due to the development of industry such as the chemical industry, the oil industry, the metallurgical industry, new sources of environmental pollution have emerged named wastewaters [1, 2]. A major challenge for researchers is finding method to treat wastewaters because these are the main sources of the environment contamination with heavy metal ions [3].

Contamination of water sources with Pb(II) ions is an problematic issue with serious ecological and human health consequences mainly because the heavy metal can not be destroyed or degraded, have a toxic effect on most life forms and also tend to accumulate in the environment [3, 4].

Various methods have been reported in literature for the removal of lead ions such as chemical precipitation, ion exchange, flocculation, electrolysis, adsorptions [5-8]. Although most of these methods have proven their effectiveness in the removing heavy metals at laboratory level, they have limited industrial applications mainly because are expensive, required complex equipments, high

energy consumption and operation time, low removal efficiency and in some cases can generate large quantities of secondary sludge, which must be also properly treated in order to prevent the environment contamination [5, 6].

Unlike the other methods, adsorption could be considered a promising alternative for removing lead ions from aqueous media due to its efficiency, high selectivity, low cost, ease of operation, simplicity, availability in a wide range of experimental conditions [7, 8]. But, all these advantages are closely related to the nature of adsorbent material used in the adsorption processes. This is the reason for that many years, many adsorbent materials obtained from natural material (clay material, yeasts, peat) or industrial waste and by-products (fly ash, plastics) have been used in literature for the adsorptive removal of heavy metal ions [7-9].

Clay materials have received increased attention, mainly because they are cheap, available in large quantities in many region of the world, and they are easy to prepare. On the other hand, clay materials have high specific area and contain on their surface a variety of functional groups which can represent the binding sites in adsorption processes [10-12].

Geologically, clay materials are defined as particles with smaller dimensions up to 2  $\mu\text{m}$ , massive or stratified rocks, characterized by high porosity [11-14]. Chemical structure of clay materials involve hydrous aluminosilicates which comprise of variety of minerals, and metal oxides ( $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{SiO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{CaO}$ ). The basic units of the clay are the networks of silicon tetrahedra and aluminum octahedra that interlock forming layers [12]. The thicknesses of these layers are in few nanometers range and length is several microns, and arranged into stacks with the gap filled with exchangeable metal cations [15, 16]. Due to these characteristics, the clay materials have excellent adsorption properties and can be successfully used for the retention of various heavy metal ions from aqueous media [17, 18].

In this study, the adsorptive potential of clay material sampled from Vlădiceni (Romania), was studied for the removal of Pb(II) ions from aqueous media. The adsorption behavior of Pb(II) ions was examined as a function of initial solution pH, adsorbent dosage, initial Pb(II) ions concentration, contact time and temperature, in order to find the optimal experimental conditions. The experimental results included in this study shows that this clay material can very quickly retain a large amount of Pb(II) ions (112.41 mg/g) and have potential to be use as adsorbent material in the decontamination processes of the environment.

## 2. Experimental

### 2.1. Adsorbent preparation

The clay material used as adsorbent in this study was sampled from Vlădiceni, Iași, Romania (geographical localization: 47° 7' 48" – N, 27° 39' 50" – S). The sample of clay material was dried in air at 60 °C for 3 hours, ground, mortared and sieved, until the particles grain-size was lower than 0.5 mm. After preparation, the clay material was stored in desiccators and was used in the adsorption experiments without any supplementary treatment.

### 2.2. Reagents

All chemical reagents used in this study were of analytical grade and were used without further purifications. A stock solution of Pb(II) ions (2055 mg Pb(II)/L) was obtained by dissolving an exact weight quantity of lead nitrate in distilled water. All working solutions were prepared from the stock solution, by dilution with distilled water. 0.1 mol/L of  $\text{HNO}_3$  and NaOH solutions were used to adjust the initial pH of working solutions.

### 2.3. Adsorption experiments

The adsorption experiments were performed in batch systems, by mixing a given quantity of clay adsorbent with 25 mL of aqueous solution with known Pb(II) ions concentration, known initial

solution pH and temperature, for a determined period of time, in 100 mL conical flask. The range of variation of the experimental parameters for each type of experiment is summarized in Table 1.

Table 1. The range of variation of the experimental parameters in the adsorption experiments.

Experiment	pH	Adsorbent dosage, g/L	Pb(II) concentration, mg/L	Contact time, min	Temperature, °C
Effect of initial solution pH	2.0 – 7.0	4.0	82.76	1440	20.5
Effect of adsorbent dosage	7.0	4.0 – 20.0	82.76	1440	21.0
Effect of initial Pb(II) concentration	7.0	4.0	20.17 – 579.33	1440	20.0
Effect of contact time	7.0	4.0	83.02; 249.07	5 – 180	21.0
Effect of temperature	7.0	4.0	20.17 – 579.33	180	10; 20; 50

All samples were shaken intermittently, over the specified time period. At the end of adsorption experiments, the phases were separated through filtration (0.45 mm quantitative filter paper), and Pb(II) ions concentration in filtrate was analyzed spectrophotometrically (Digital Spectrophotometer S104 D, 1 cm glass cell, color reagent: 4-(2-piridilazo)-resorcinol,  $\lambda = 530$  nm), using a prepared calibration graph.

The adsorption capacity of clay material ( $q$ , mg/g) and the removal percent of Pb(II) ions from aqueous solution ( $R$ , %), were calculated using the following equations:

$$q = \frac{(c_0 - c) \cdot V}{m} \quad (1)$$

$$R = \frac{c_0 - c}{c_0} \cdot 100 \quad (2)$$

where:  $c_0$  and  $c$  are the initial and equilibrium Pb(II) ions concentration in solution (mg/g);  $V$  is a measure of solution (L), and  $m$  is the mass of clay material (g).

### 3. Results and discussion

In all cases, the adsorption process of the given metal ion on a given adsorbent material has maximum efficiency only under well-defined experimental conditions, which depend on the nature of these two components [19, 20]. Therefore, the first step in characterizing an adsorption process is to establish the optimum experimental conditions, which ensure maximum efficiency.

Five experimental parameters, namely: initial solution pH, adsorbent dosage, initial metal ions concentration, contact time and temperature, are examined for this purpose, and the optimal value of each parameter is considered that for which the adsorption capacity ( $q$ , mg/g) and/or removal percent ( $R$ , %) are the highest.

#### 3.1. Effect of initial solution pH

The pH of the initial solution is one of the most important experimental parameters that influence the efficiency of a given adsorption process, since its value affects both the speciation of the metal ions in aqueous solution and the superficial properties of the adsorbent material [21, 22].

In this study, the effect of initial solution pH was studied in the pH interval of 2.0 – 7.0, at a constant Pb(II) ions concentration, adsorbent dosage, contact time and temperature (see Table 1), and the obtained experimental results are illustrated in Fig. 1.

As can be observed from Fig. 1, the amount of Pb(II) ions retained on mass unit of clay adsorbent increase with the increasing of initial solution pH, in the interval between 2.0 and 4.0, from 7.73 to 18.09 mg/g, after that remains almost constant, even if the solution pH increase with 3 units (19.08 mg/g). This variation is mainly determined by the variation of the dissociation degree of the functional

groups from the surface of the clay adsorbent, because in the studied pH range the lead speciation is not modified.

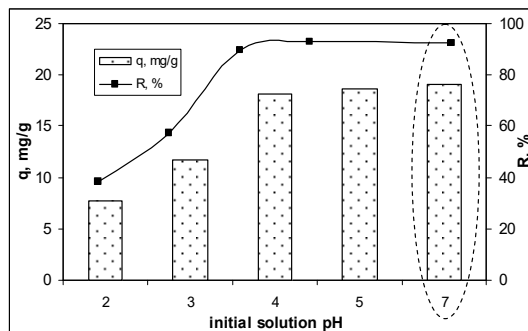


Fig. 1. Effect on initial solution pH on Pb(II) ions adsorption on clay adsorbent.

In acid media (pH=2.0), the dissociation degree of superficial functional groups is low, most of these are in the un-dissociated form, and can not interact with Pb(II) ions due to the lack of electrostatic affinity. As the pH of the initial solution increases, the dissociation degree of the surface functional groups increases, the adsorbent surface of the clay becomes negative, and the retention efficiency Pb(II) ions increases due to the electrostatic attraction. At initial solution pH higher than 4.0, probably almost all superficial functional groups of clay adsorbent are dissociated, and the amount of Pb(II) ions retained will depends only by the initial Pb(II) ions concentration from aqueous solution. When Pb(II) ions concentration is constant, the obtained values of adsorption capacity are almost the same (see Fig. 1). A similar tendency can be observed and in the case of the removal percent (Fig.1), where at initial solution pH higher than 4.0, the differences between obtained values are lower than 0.3 %.

Under these conditions, the best adsorptive performances of clay adsorbent for Pb(II) ions from aqueous solution were obtained at initial solution pH of 7.0, and this value was considered as optimal and used in all further experiments.

### 3.2. Effect of adsorbent dosage

The influence of adsorbent dosage on the adsorption of Pb(II) ions from aqueous solution was studied using different amount of clay adsorbent (see Table 1), while the other experimental parameters were maintained constant. The obtained results are presented in Fig. 2.

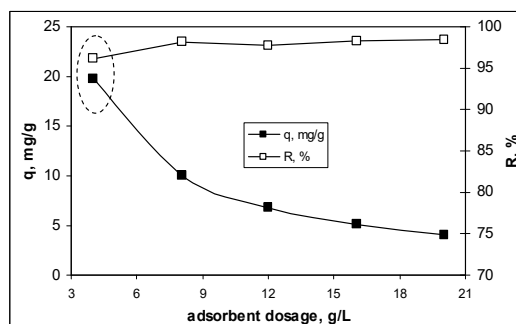


Fig. 2. Effect on adsorbent dosage on Pb(II) ions adsorption on clay adsorbent.

The experimental results indicate that the increase of the adsorbent dosage between 4.0 and 20.0 g/L determined a decrease of adsorption capacity from 19.73 to 4.07 mg/g. In the same adsorbent dosage range the values of removal percent increase very slowly, from 96.13 to 98.38 %. This

opposite variation of these two parameters is mainly due to the decrease of the number of active sites as the adsorbent dosage increased, and it is a consequence of the particle agglomeration phenomenon, reported in many studies in literature [22, 23]. The increase of clay adsorbent over 0.5 g/25 mL (20.0 g/L) did not display an additional increase of the Pb(II) ions adsorption efficiency, probably due to the saturation of the adsorbent surface.

Therefore, it was established that a dosage of clay adsorbent of 4.0 g/L can be considered optimal for the removal of Pb(II) ions from aqueous solution, and this value was used in all experiments.

### 3.3. Effect of contact time and kinetic modelling

The influence of contact time on Pb(II) ions adsorption on clay adsorbent, at a constant initial solution pH (7.0), adsorbent dosage (4.0 g/L) and room temperature (21 °C) is illustrated in Fig. 3. As is mentioned in Table 1, the initial Pb(II) concentration is 83.02 mg/L and 249.07 mg/L, respectively.

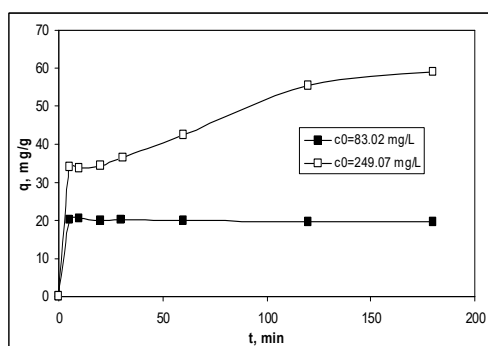


Fig. 3. Effect of contact time on Pb(II) ions adsorption on clay adsorbent.

The experimental results presented in Fig. 3 show that the Pb(II) ions adsorption efficiency on clay adsorbent increase with the increasing of contact time and reach the maximum after 5 min at low initial Pb(II) ions concentration (83.02 mg/L), while at high initial Pb(II) ions concentration (249.07 mg/L) a time period of 120 min is necessary. In the mentioned time intervals, the removal percents of Pb(II) ions are higher than 80 % and 91 %, respectively. The differences between the values of adsorption capacities obtained in these conditions and those obtained for 24 hours of contact time are lower than 3 %, as can be observed from Table 2.

Table 2. The difference between q values obtained at mentioned time period and after 24 hours.

$c_0$ , mg Pb(II)/L	t, min	$q_t$ , mg/g	$q_{24 \text{ h}}$ , mg/g	$\Delta q$ , %
83.02	5	20.27	19.79	2.42
249.07	120	33.99	35.02	2.94

Thus, to be sure that the Pb(II) ions adsorption on clay adsorbent reaches the equilibrium state, a contact time of 180 min was considered sufficient and was used in the other experimental studies.

The experimental results were analyzed using pseudo-first order and pseudo-second order kinetic models, and the best fit model was selected based on the values of regression coefficients ( $R^2$ ). The mathematical equations and the kinetics parameters obtained from linear representations of these two models (Fig. 4), for both values of initial Pb(II) ions concentration, are summarized in Table 3.

As can be observed from Fig. 4 and Table 3, the pseudo-first order model has a limited applicability in describing the experimental kinetics data, since the regression coefficients are lower ( $R^2 < 0.83$ ) and the equilibrium adsorption capacities, calculated from the model equation ( $q_{\text{calc}}^e$ , mg/g), are much different from the experimental values ( $q_{\text{exp}}^e$ , mg/g).

Compared to this, the pseudo-second order kinetic model is more suitable for describing the experimental kinetic data. The high value of correlation coefficients ( $R^2 > 0.99$ ), and the close values

of adsorption capacity, calculated from this model equation ( $q_{calc}^e$ , mg/g) and obtained experimentally ( $q_{exp}^e$ , mg/g), show that the adsorption of Pb(II) ions from aqueous solution on clay adsorbent follow this kinetic model.

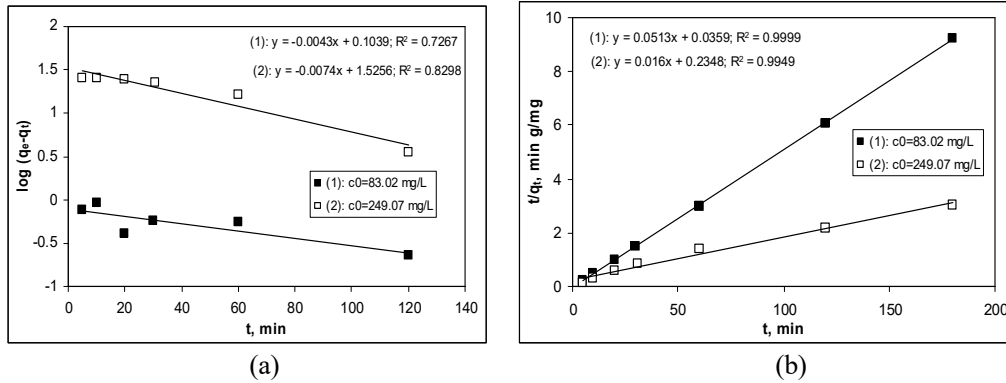


Fig. 4. Linear representations of the pseudo-first order (a) and pseudo-second order (b) kinetics models for Pb(II) ions adsorption on clay adsorbent.

Table 3. The values of kinetic parameters obtained for Pb(II) adsorption on clay adsorbent.

Kinetic model	Mathematical equation [24, 25]	Parameters	$c_0 = 83.02 \text{ mg/L}$	$c_0 = 249.07 \text{ mg/L}$
		Pseudo-first order model	$\log(q_e - q_t) = \log q_e - k_1 \cdot t$	$q_{exp}^e$ , mg/g
$R^2$	0.7267			0.8298
$q_{calc}^e$ , mg/g	1.2703			33.5428
$k_1$ , 1/min	0.0043			0.0074
Pseudo-second order model	$\frac{t}{q_t} = \frac{1}{q_e^2 \cdot k_2} + \frac{t}{q_e}$	$R^2$	0.9999	0.9949
		$q_{calc}^e$ , mg/g	19.4931	62.5000
		$k_2$ , g/mg min	0.07331	0.0011

The very good correlation of the experimental data with the pseudo-second order kinetic model indicates that in the adsorption of Pb(II) ions on clay adsorbent, the rate controlling step is the chemical interaction, probably ion exchange type, between metal ions from aqueous solution and functional groups of clay adsorbent. These interactions require two binding sites with favorable geometric positions, and therefore only the functional groups on the clay adsorbent surface will be involved in the adsorption process [25]. This assumption is supported and by the values of rate constant ( $k_2$ , g/mg min) which increase with the increasing of initial Pb(II) ions concentration. This means that at high initial Pb(II) ions concentration, the interactions between metal ions and functional groups from clay adsorbent surface occur more quickly, even if it takes longer to reach the equilibrium state.

### 3.4. Effect of initial Pb(II) ions concentration and temperature

The influence of initial Pb(II) ions concentration on the adsorptive performances of clay adsorbent was examined at three different values of temperature (10, 20 and 50 °C), under optimized experimental conditions (initial solution pH of 7.0, 4.0 g/L adsorbent dosage and 180 min of contact time) (see Table 1). The obtained experimental results are presented in Fig. 5.

As can be seen from Fig. 5, the adsorption capacity of clay adsorbent increases with the increase of initial concentration of Pb(II) ions, for all studied values of temperature. Thus, at 20 °C, the increase of initial Pb(II) ions concentration from 20.17 to 579.33 mg/L determines a increase of the adsorption capacity of clay adsorbent from 20.15 to 73.71 mg/g, for 3 hours of contact time.

The increase of the adsorption capacity ( $q$ , mg/g) with the increase of the initial concentration of Pb(II) ions is mainly determined by the increase of the probability of collision between the metal ions and the superficial functional groups of the adsorbent, which represents the driving force of the adsorption process [26].

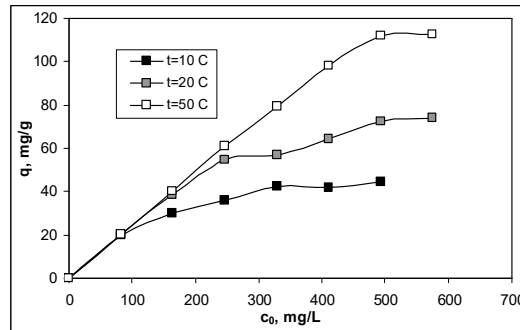


Fig. 5. Effect of initial metal ions concentration and temperature on Pb(II) ions adsorption on clay adsorbent.

On the other hand, the experimental results presented in Fig. 5 shows that the efficiency of the adsorption process also depends significantly on the temperature. Increasing the temperature from 10 to 50 °C, causes an increase of the adsorption capacity on the entire studied initial Pb(II) ions concentration, and this is evident especially in the high initial Pb(II) ions concentration range. Thus, at highest initial Pb(II) ions concentration of 575.46 mg/L, the adsorption capacity increase from 61.11 mg/g at 10 °C, to 112.42 mg/g at 50 °C (see Fig. 5). These observations indicate that the adsorption process of Pb(II) ions on clay adsorbent has an endothermic nature, and that the increase of temperature provide the energy to overcome all barriers, thus facilitating the interactions between the metal ions and the functional groups of the adsorbent [25, 26].

### 3.5. Modelling of experimental isotherms

The quantitative description of the adsorption process of Pb(II) ions on clay adsorbent can be done by modeling the experimental adsorption isotherms, and in this study, this was done using the Langmuir and Freundlich isotherm models, for all the studied temperatures.

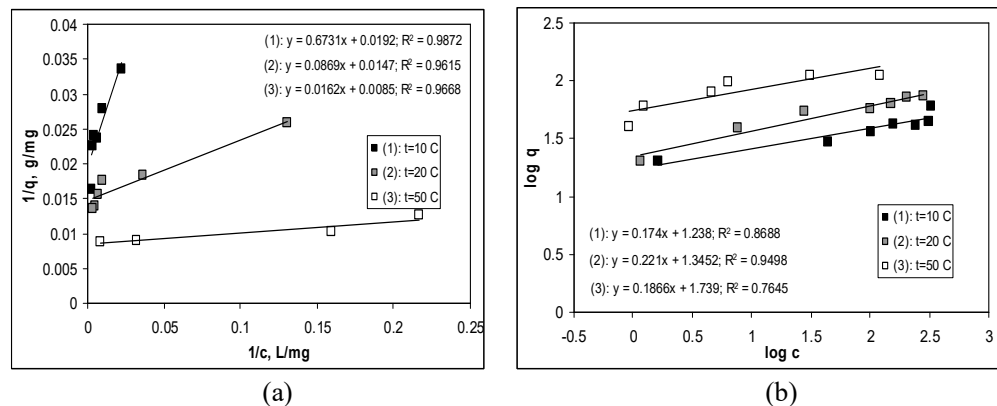


Fig. 6. Linear representations of the Langmuir (a) and Freundlich (b) isotherm models for Pb(II) ions adsorption on clay adsorbent.

The mathematical equations of these two models and the isotherm parameters obtained from linear representations characteristic of each model (Fig. 6), are presented in Table 4. And in this case, the best fit model was selected considering the values of regression coefficients ( $R^2$ ), obtained from linear regression.

Table 4. The values of isotherm parameters obtained for Pb(II) adsorption on clay adsorbent.

Isotherm model	Mathematical equation [25, 26]	Parameters	10 °C	20 °C	50 °C
Langmuir model	$\frac{1}{q} = \frac{1}{q_{\max}} + \frac{1}{q_{\max} \cdot K_L} \cdot \frac{1}{c}$	$R^2$	0.9872	0.9615	0.9668
		$q_{\max}$ , mg/g	52.0833	68.0272	117.6471
		$K_L$ , L/g	0.0285	0.1692	0.5247
Freundlich model	$\log q = \log K_F + \frac{1}{n} \log c$	$R^2$	0.8688	0.9498	0.7645
		1/n	0.1740	0.2210	0.1866
		$K_F$ , L/g	17.2981	22.1411	54.8276

Comparison of the values of regression coefficients ( $R^2$ ) indicates that the Langmuir isotherm model best describe the experimental data obtained for Pb(II) ions adsorption on clay adsorbent for all studied temperatures, than the Freundlich isotherm model. Therefore, the adsorption process occurs until a monolayer coverage of Pb(II) ions is formed on the external surface of clay adsorbent, after that after saturation is reached. The maximum adsorption capacity ( $q_{\max}$ , mg/g) increase with the increasing of temperature (Table 4), and the obtained values are close to the experimental ones. This means that most of the superficial functional groups of clay adsorbent are available to interact with Pb(II) ions from aqueous solution, and almost all are occupied during of adsorption process. In addition, the high values of Langmuir constant ( $K_L$ , L/g), indicate that the retention of Pb(II) ions on clay adsorbent occurs through strong interactions.

On the other hand, the values of the Langmuir model parameters increase with increasing temperature (see Table 4). This variation indicate that: (i) the adsorption process of Pb(II) ions on clay adsorbent is endothermic, and (ii) the high values of temperature facilitated the interactions between metal ions from aqueous solution and functional groups of adsorbent, and in consequence the saturation state is reached at higher Pb(II) ions concentrations, as the higher is the temperature (see Fig. 5). All these observations highlight the possibility of using this clay adsorbent to remove Pb(II) ions from hot aqueous media.

#### 4. Conclusions

In this study was examined the removal of Pb(II) ions from aqueous media using as adsorbent a low-cost clay material, which is locally available. The adsorption experiments were performed in batch systems, and the obtained results have indicate that the highest adsorption capacity of clay adsorbent is obtained at initial solution pH of 7.0, 4.0 g/L adsorbent dosage, 3 hours of contact time and high temperature (50 °C). Under these conditions, more than 99 % from Pb(II) ions are retained on clay adsorbent, at an initial metal ions concentration lower than 310 mg/L. The pseudo-second order kinetic model is the most adequate in describing the kinetics of adsorption process, while the equilibrium experimental data were best fitted by the Langmuir isotherm model. The values of rate constant ( $k_2$ , g/mg min) increase with the increasing of initial Pb(II) ions concentration, which means that at high initial Pb(II) ions concentration, the interactions between metal ions and functional groups from clay adsorbent surface occur more quickly, even if it takes longer to reach the equilibrium state. The maximum adsorption capacity ( $q_{\max}$ , mg/g) increase with the increasing of temperature, indicating that the high values of temperature facilitated the interactions between metal ions from aqueous solution and functional groups of clay adsorbent. All the experimental results included in this study, highlight the practical applicability of this clay material as adsorbent in the decontamination processes of the environment.

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