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Efficient Removal of Toxic Metal Ions (Pb(II) and Hg(II) Ions in Single Component Systems by Adsorption on Romanian Clay Material

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Abstract: *In this study, a local natural clay material was used for the efficient removal of Pb(II)ions and Hg(II) ions from aqueous media, in batch system. The adsorptive potential of clay material was testes at different initial solution pH, adsorbent dosage, contact time and initial heavy metal ions concentration and room temperature (20 ± 2℃). The highest adsorption efficiency of clay material was found at initial pH of 7.0 in case of Pb(II) ions, and 2.0 in case of Hg(II) ions, while the adsorbent dosage had the same value (4 g/L) for both metal ions. The adsorption equilibrium is very fast and was reach within 10 min. The modelling of experimental data showed that the adsorption processes followed the Freundlich isotherm model and pseudo-second order kinetic model. Detailed analysis of the experimental data indicate that the retention of Pb(II) and Hg(II) ions from aqueous solution on clay materials involves two processes, one of adsorption and the other of precipitation, whose succession depends on the speciation form of the metal ion in aqueous solution. However, the high adsorption capacity and short contact time are important characteristics which suggest the potential use of this clay material in environmental remediation processes.*

Keywords*: toxic metal ions, clay material, adsorption, aqueous media, environmental remediation*

1. Introduction

The high content of heavy metals in industrial wastewater represents a significant hazard to the quality of life of people around the world, mainly due to their non-biodegradability and their tendency to accumulate through the food chain. The presence of toxic heavy metal ions, such as Pb(II), Hg(II), Cd(II), Cr(VI), As(III/V), etc., in water sources, is considered a major risk factor, which affect both the human health and the quality of ecosystems. Among these, Pb(II) and Hg(II) ions are extremely toxic, and humans exposure to these metal ions causes kidney diseases, liver and cardiovascular dysfunction or irreversible brain damage [1, 2]. In consequence, the presence of such metal ions in ground and surface waters should be avoided over a maximum concentration limit, in accordance with the recommendations of the World Health Organization [3].

The main sources of water pollution with such toxic metal ions are the industrial effluents, resulted from various industrial sections (such as electroplating, fertilizers manufacturing, batteries manufacturing, paints fabrications, etc.) [4-6]. Incomplete or inefficient treatment of these effluents during technological processes, followed by their discharge into the environment are mainly responsible for the contamination of water sources with this kind of pollutants. Therefore, finding a suitable treatment process, customized for each type of wastewater, is still a priority in current environmental research [6, 7].

Until now, several treatment methods such as precipitation, flotation, coagulation, membrane separation, ion exchange, various electrochemical techniques, adsorption, etc. [6-9], have been used

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**email: lbulg@ch.tuiasi.ro, dbulgariu@yahoo.com* for the removal of Pb(II) and Hg(II) ions from different effluent matrices, on an industrial scale. Most of these methods have some important limitations related to their high operation costs, disposal problems of obtained sludge, low efficiency in the treatment of huge volume of wastewater, etc. [10, 11]. On the other hand, the removal of metal ions from industrial effluents by adsorption has proven to be more economic and efficient. This is why, in recent years, finding a suitable adsorbent material, which is abundant, ecologic, easy to prepare and stable over time, has become a priority. All these conditions are fully fulfilled by natural materials.

Natural materials are available in large quantities, which cause their price to be lowered and, most of the time, their preparation involves only a few simple mechanical operations designed to reduce the size of their particles [11, 12]. Thus materials such as peat, zeolites, different types of coal, minerals and clay minerals, etc., have been used in literature [12-15] for the retention of different heavy metal ions (including Pb(II) and Hg(II)) from aqueous effluents, and in most of these studies, their potential applicability in treating industrial wastewater was highlighted. Among the natural materials, clays have been proved to be the most efficient for this purpose, due to their high adsorptive performances [16]. According to Kausar et al. [17], the high adsorptive performances of clay materials can be attributed both to the high number of negative charges from the clay surface, which makes that the positively charged ions to be attracted, and to the large surface area (up to 800 m^2/g), due to their high porosity and the small size of the clay particles.

Romania, like many other regions of the world, has a great variety of clay minerals, which are extracted and used as raw material in different industrial sectors. An important deposit of such clay minerals is located in the SE part of Iasi [18]. The clays from this region are characterized by a high content of SiO_2 and iron, and these particularities give them high adsorbent properties, due to the possibility of forming on their surface a large number of binding sites [19]. This is why this clay material has been used in our adsorption studies.

Therefore, in this study, the adsorptive potential of clay material sampled from Vladiceni (SE part of Iaşi, Romania) was examined for the removal of toxic heavy metal ions (Pb(II) and Hg(II)) from aqueous media. The experimental research focused on the effect of the *p*H of the initial solution, the adsorption dose, the contact time and the initial concentration of heavy metal ions on the adsorption efficiency. Isotherm and kinetic modelling was done to understand the mechanism of adsorption processes. The experimental results of this study indicate that this clay material can very quickly remove large amounts of Pb(II) and Hg(II) ions, by a complex mechanism involving adsorption and precipitation.

2. Materials and methods

2.1. Materials

Clay material was sampled from Vladiceni (Iaşi, Romania) from the surface horizon (10 – 40 cm). The main chemical and mineralogical components of this material are presented in Table 1.

Table 1. The main chemical and mineralogical components of clay material used as adsorbent

Chemical component		**Mineral component**	
Component	**Value (%)**	**Component**	**Value (%)**
SiO_2	60.37	Smectite	5.93
Al_2O_3	14.65	Illite	8.27
Fe_2O_3	3.82	kaolinite	67.75
CaO	8.19	Iron oxydes	2.07
MgO	1.13	Sulphates	1.29
Na_2O	2.58	Carbonates	10.58
K2O	1.96	Organic matter	0.24

Before utilization in experimental studies, the clay material was dried in air at 60°C for 6h, ground, mortared and sieved. Only fractions with a grain size of less than 0.5 mm were stored in desiccators for adsorption experiments. The characterization of the clay adsorbent was done by FTIR spectrometry and SEM microscopy. FTIR spectra were recorded in 400 – 4000 cm^{-1} spectra domain, using a Bio-Rad FTIR spectrometers, by KBr disk technique, to highlight the nature of functional groups from adsorbent surface. SEM images (SEM-Hitach S3000N microscope) were recorded to determine changes in the surface morphology of the adsorbent.

Lead nitrate and mercury nitrate salts (purchased from Chemical Company, Romania) was used to prepare the stock solutions (10^{-2} mol M(II)/L), by dissolving known amounts of salts in distilled water. The working solutions with different concentrations of metal ions were obtained by appropriate dilution of the stock solutions. *p*H of the working solutions was adjusted with 0.1 mol/L HNO_3 solution, and measured with a *p*H/ion-meter MM-734 types, equipped with a combined glass electrode and conductometric cell.

2.2. Adsorption studies

Adsorption studies of Pb(II) and Hg(II) ions onto clay material were conducted in batch systems, at room temperature (20 ± 2 °C). The influence of initial solution *p*H (2-7), adsorbent dosage (4-20 g/L), contact time (5-180 min) and initial metal ions concentration (0.1-2.8 mmol/L) were examined in single component systems, analyzing each factor one by one. In each case, 25 mL of heavy metal ions solution were intermittent stirred with a known amount of clay material for a certain period of time (24 hours, except the kinetic studies) under well-established experimental conditions. After equilibration, the solid and liquid phases were separated by filtration (quantitative filter paper) and the obtained solution was used to determine the concentration of heavy metal ions. The concentration of each metal ion in filtrate was spectrophotometrically analyzed (Digital Spectrophotometer, S104 D, 1 cm glass cell), in the following conditions: for Pb(II) ions: colour reagent: 4-(2-piridilazo)-resorcinol, $\lambda = 530$ nm, against blank solution, for Hg(II) ions: colour reagent: methyl blue thymol, $\lambda = 610$ nm, against distilled water, by interpolation from the calibration curves [20].

The adsorption capacity of clay material and the percent of heavy metal ions removal were calculated using the following equations:

$$q = \frac{(c_0 - c)\cdot(V/1000)}{m} \tag{1}$$

$$R = \frac{c_0 - c}{c_0}\cdot 100 \tag{2}$$

where: c_0 and c are initial and equilibrium concentration of heavy metals in solution (mmol/L), V is volume of solution (mL), and m is the mass of biosorbent (g).

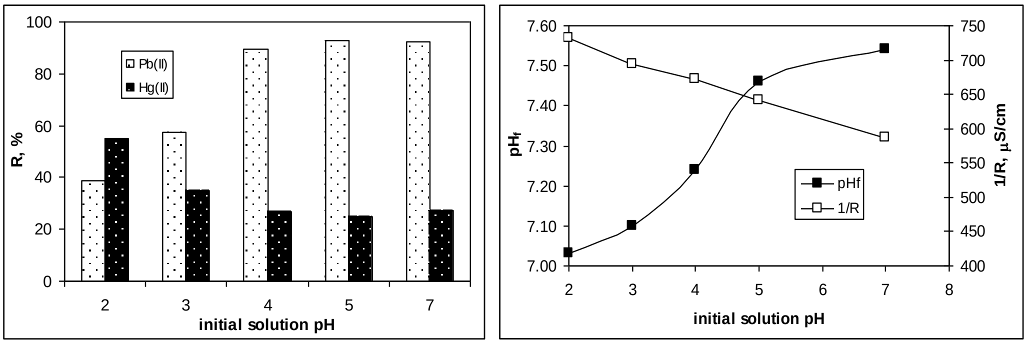
3. Results and discussions

3.1. Effect of initial solution *p*H

The initial solution *p*H is one of the most important parameters that affect the efficiency of the adsorption processes on clay materials [21, 22], mainly because it is responsible for both the speciation form of metal ion in aqueous solution, and the dissociation of functional groups from adsorbent surface. This is the reason why in this study, the adsorptive performances of clay materials were examined using toxic heavy metal ions solutions (Pb(II) and Hg(II)) with different initial *p*H values, ranging from 2.0 to 7.0, and the obtained experimental results are presented in Figure 1. The initial *p*H of the solutions used in these experiments was not higher than 7.0, to avoid the bulk precipitation of metal ions in the aqueous solution.

It can be seen from Figure 1a that the adsorption efficiency of both toxic heavy metal ions (Pb(II) and Hg(II)) is strongly influenced by the initial solution *p*H. The adsorption efficiency increases from 38.50 to 95.63 % for Pb(II) with the increase of the initial *p*H values from 2.0 to 7.0, while in the case of Hg(II) ions the adsorption percents decrease from 54.86 to 27.28 %, in the same *p*H interval. Therefore, the highest metal ions removal percents are obtained at *p*H 7.0 in case of Pb(II) ions, and at *p*H 2.0 in case of Hg(II) ions, and these values were considered as optimal and used in the further experiments.

This opposite variation of the removal percents obtained in case of Pb(II) and Hg(II) ions adsorption is mainly due to the physico-chemical properties of clay material. Thus, it was observed that, after adsorption the final solution *p*H (pH_f) is higher than 7.0, regardless of its initial value (Figure 1b). The *p*H values of the final solutions higher that 7.0 show that in this case in the removal of heavy metal ions from aqueous solution, in addition to the adsorption process, their precipitation has an important contribution. The simultaneous development with the adsorption process of a precipitation process, most probably on the surface of the clay material, is also supported by the electrical conductivity (1/R) measurements (Figure 1b). The decrease of the values of this parameter over the entire studied *p*H range shows during the adsorption process there is a decrease of the concentrations of ionic species in the solution, and this is due to the superficial precipitation and not to the ion exchange.



(a) (b)

Figure 1. (a) Effect of initial solution *p*H on adsorption efficiency of Pb(II) and Hg(II) on clay material. (b) Variation of final solution *p*H (pH_f) and electrical conductibility (1/R) in function of initial solution *p*H

The alkaline characteristics of clay material can be explained considering the nature of the functional groups that are found on its surface. FTIR spectra recorded for clay material (Figure 2) show that the main superficial functional groups of this material are: O–H from water molecules (3625 cm^{-1}), Al–O and Mg–O (3402-3431 cm^{-1}), Si–O (1024 cm^{-1}) and water molecules from internal structure of clay mineral (1639 cm^{-1}) [23, 24].

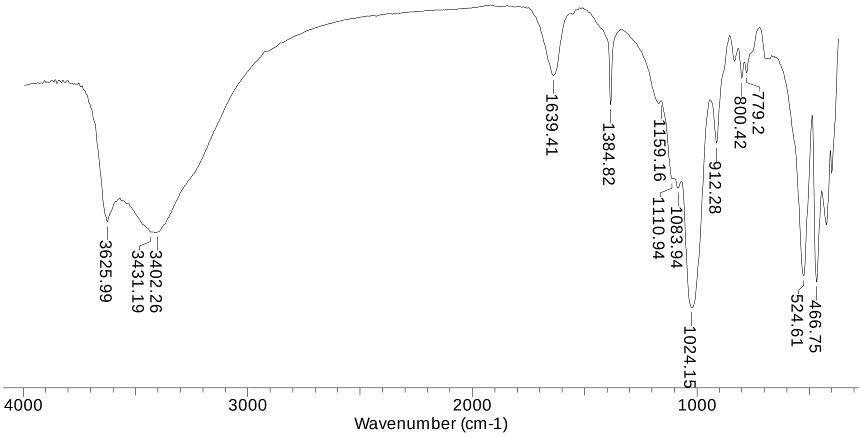
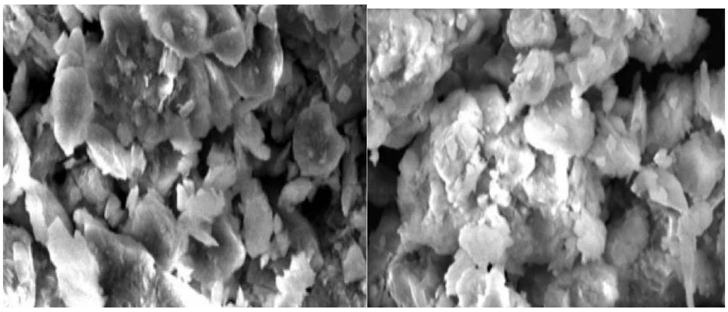


Figure 2. FTIR spectra of clay material used as adsorbent in this study

When the clay material is brought into contact with the aqueous solution of heavy metal ions, its surface is hydrated, and the functional groups become alkaline (Si–OH, Al–OH, Mg–OH, etc.) [25]. This causes the significant increase of *p*H at the surface of the clay material. Consequently, heavy metal ions in aqueous solution will be attracted to the surface of the clay material, mainly due to the high pH which gives them greater stability due to precipitation.

Precipitation of heavy metal ions on the surface of the clay material can be clearly seen from the SEM images. For exemplification in Figure 3 are presented the SEM images recorded for clay material before and after Pb(II) ions retention. Thus it can be observed that after Pb(II) ions retention, the surface of clay material is covered with a layer of precipitate and becomes smoother.



(a) (b)

Figure 3. SEM images of clay material before (a) and after (b) retention of Pb(II) ions from aqueous solution (2500X)

Unlike Pb (II) ions, Hg (II) ions remain as free cations in solution only at low *p*H values [26]. When the initial solution *p*H increase, their precipitation in solution takes place, and thus they no longer reach the surface of the clay material. Consequently, the retention efficiency of Hg (II) ions decreases with increasing of initial solution *p*H, as can be seen in Figure 1a.

3.2. Effect of adsorbent dosage

In order to study the influence of adsorbent dosage on the adsorption efficiency of Pb(II) and Hg(II) ions from aqueous solution, the amount of clay material was varied from 4.0 to 20.0 g/L, and the obtained results are presented in Figure 4.

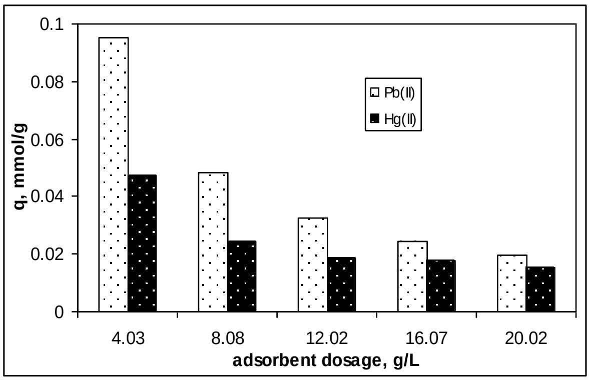


Figure 4. Effect of adsorbent dosage on the adsorption efficiency of Pb(II) and Hg(II) ions on clay material (initial *p*H = 7.0 (Pb(II) and 2.0 (Hg(II), c_0 = 0.40 mmol M(II)/L, contact time = 24 h)

The obtained experimental results (Figure 4) shows that the adsorption capacities of clay materials decrease with the increase of the adsorbent dosage, from 0.095 to 0.019 mmol/g in case of Pb(II) ions, and from 0.047 to 0.015 mmol/g in case of Hg(II) ions, respectively. The decrease of adsorption capacity (q, mmol/g) with the increase of the adsorbent dosage derives from the mathematical equation of this parameter (eq. (1)). Even if with the increase of the adsorbent dosage, the amount of retained metal ions increases, reporting to high values determines the obtaining of lower values for the adsorption capacity. Similar variations have been also reported in many studies from literature [22, 24, 27, 28]. Therefore, an adsorbent dosage of 4.0 g/L was considered optimal for the removal of Pb(II) and Hg(II) ions from aqueous solution by adsorption on clay material, and this value was used in all further experiments.

3.3. Effect of contact time and kinetic modelling

The influence of contact time on the adsorption efficiency of clay materials for the removal of Pb(II) and Hg(II) ions from aqueous media, was analyzed in the time interval between 5 and 180 min, as shown in Figure 5.

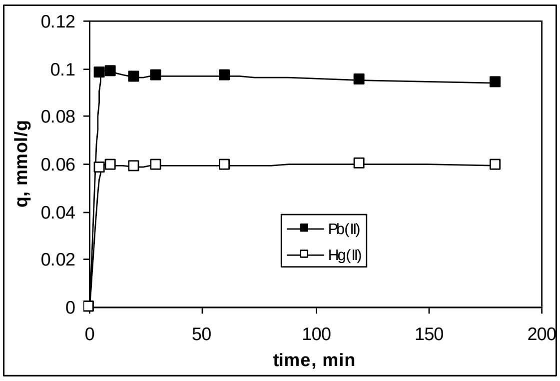


Figure 5. Influence of contact time for the adsorption of Pb(II) and Hg(II) on clay material (initial pH = 7.0 (Pb(II) and 2.0 (Hg(II), adsorbent dosage = 4.0 g/L, c_0 = 0.40 mmol M(II)/L)

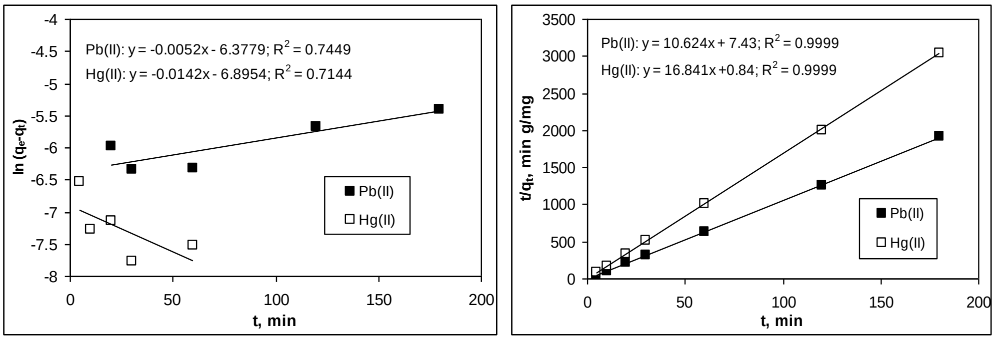
A very fast increase in the adsorption capacity of clay material can be observed for both heavy metal ions (Pb(II) and Hg(II)) in the first 10 min, after which the adsorption capacity increases very slowly with increasing of contact time. Thus, after 10 min of contact time, the adsorption process can be considered at equilibrium, and the experimental values of adsorption capacity are 0.098 mmol/g in case of Pb(II) and 0.059 mmol/g in case of Hg(II), respectively. The low value of constant time required to reach equilibrium is mainly determined by the presence of a large number of adsorption sites on the surface of clay material, which are initially free and can easily bind the heavy metal ions from aqueous media.

Quantitative description of the kinetics of adsorption processes was performed by modelling the experimental data, using pseudo-first order and pseudo-second order kinetics models. The mathematical equations of these two models are [29, 30]:

Pseudo-first order model: $\ln(q_e - q_t) = \ln q_e - k_1 \cdot t$ (3)

Pseudo-second order model: $\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{t}{q_e}$ (4)

where: q_e, q_t – adsorption capacity at equilibrium and at time t; k_1 - rate constant of pseudo-first order model; k_2 - rate constant of pseudo-second order model.



(a) (b)

Figure 6. Linear representations of pseudo-first order (a) and pseudo-second order (b) kinetics models for the adsorption of Pb(II) and Hg(II) ions on clay material

The linear representation of the pseuso-first order model (ln(q_e-q_t) vs. t) and of the pseudo-second order model (t/q_t vs. t) are illustrated in Figure 6, while the kinetic parameters, calculated for each metal ion, are summarized in Table 2.

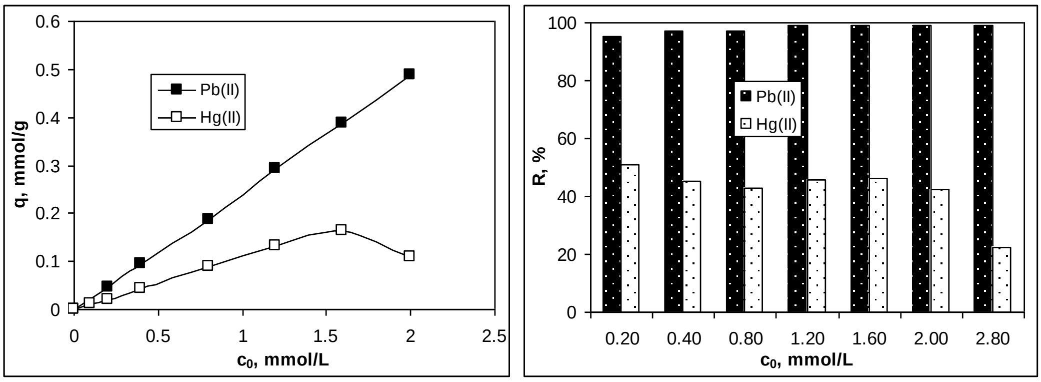
Table 2. Kinetic parameters for the adsorption of Pb(II) and Hg(II) on clay material

Kinetic model	**Parameters**	**Pb(II)**	**Hg(II)**
Pseudo-first order	R^2	0.7449	0.7144
	q_e^{calc} (mmol/g)	0.0017	0.0011
	k_1 (1/min)	0.0052	0.0142
Pseudo-second order	R^2	0.9999	0.9999
	q_e^{calc} (mmol/g)	0.0971	0.0594
	k_2 (g/mmol min)	15.1976	3.3783

It can be observed from Figure 6 and Table 2 that the pseudo-second order kinetic model describe the kinetics of adsorption processes with greater accuracy ($R^2 \approx 1$), compared with the pseudo-first order kinetic model ($R^2 < 0.75$). In addition, the adsorption capacities calculated for this model are comparable with the experimental values (0.098 mmol/g for Pb(II); 0.059 mmol/g for Hg(II)). All these observations demonstrate that in the studied adsorption processes, the binding of heavy metal ions (Pb(II) and Hg(II)) involves chemical interactions with the superficial functional groups or electron sharing [30, 31]. Therefore, the limiting step in the adsorption of Pb(II) and Hg(II) ions on the clay material are the chemical interactions with the superficial functional groups, which means that the efficiency of these processes will depend very much on the experimental conditions in which they take place.

3. 4. Effect of initial metal ions concentration and isotherm modelling

Initial heavy metal ions concentration (Pb(II) and Hg(II)) was varied between 0.1 and 2.8 mmol/L, and the effect of this parameter on the efficiency of adsorption processes is illustrated in Figure 7.



(a) (b)

Figure 7. Effect of initial heavy metal ions concentration on the adsorptive performances of clay material ((a) – adsorption capacity; (b) – removal percent) (initial *p*H = 7.0 (Pb(II) and 2.0 (Hg(II), adsorbent dosage = 4.0 g/L, contact time = 24 h)

The experimental results (Figure 7) show that the increase of initial concentration of heavy metal ions determines an increase of the adsorption capacity over the entire concentration interval in case of Pb(II) ions (from 0.05 to 0.69 mmol/g), while in case of Hg(II) ions adsorption, the adsorption capacity increases only up to 1.6 mmol/L (from 0.01 to 0.16 mmol/g), after which it decreases (to 0.10 mmol/g). In addition, if in the case of Pb(II) ions, its adsorption is quantitative regardless of the value of the initial concentration (R > 97 %), in case of Hg(II) ions, the removal percents do not exceed 55%, even at low concentrations. This difference in the adsorption behaviour of these two ions is mainly caused by the alkaline characteristics of the clay material used as adsorbent in this study. The significalty increase of the solution *p*H after the addition of clay material (section 3.1) makes that in the retention process of heavy metal ions, in addition to adsorption, precipitation has an important role. Thus, in case of Pb(II) ions, which are present in solution as free ions up to *p*H around 6.0 [20], their retention involves first binding to the functional groups of the adsorbent, and then saturation of the free valences with basic groups from solution. In case of Hg(II) ions, which are present in solution in the free form up to *p*H less than 2.0 [26], first precipitation takes place, and then the remaining metal ions reach the vicinity of the functional groups of the clay material and are retained by adsorption.

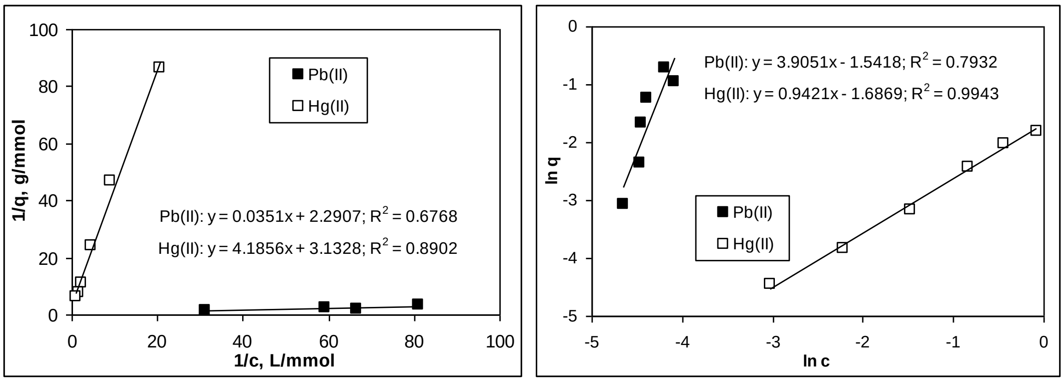
The modelling of the experimental isotherms obtained at the adsorption of Pb(II) and Hg(II) ions on clay material was done using Langmuir and Freundlich isotherm models. The selection of these two isothermal models was made taking into account that the Langmuir model describes a monolayer adsorption on the surface of the adsorbent material, while the Freundlich model indicates that the retention of metal ions takes place in several layers [32, 33]. The mathematical equation of these two models are:

$$\text{Langmuir model: } \frac{1}{q} = \frac{1}{q_{\max}} + \frac{1}{q_{\max} \cdot K_L} \cdot \frac{1}{c} \qquad (5)$$

$$\text{Freundlich model: } \ln q = \ln K_F + \frac{1}{n} \ln c \qquad (6)$$

where: q – adsorption capacity at equilibrium, q_{max} - maximum adsorption capacity, K_L - Langmuir constant, K_F - Freundlich constant, n - heterogeneity factor.

The linear representations of Langmuir (1/q vs. 1/c) and Freundlich (ln q vs. ln c) isotherm models for the adsorption of Pb(II) and Hg(II) ions on clay material are illustrated in Figure 8, and the isotherm parameters calculated for each model are summarized in Table 3.



(a) (b)

Figure 8. Linear representation of Langmuir (a) and Freundlich (b) isotherm models for the studied adsorption systems.

Table 3. Isotherm parameters for the adsorption of Pb(II) and Hg(II) on clay material

Isotherm model	Parameters	Pb(II)	Hg(II)
Langmuir model	R^2	0.6768	0.8902
	q_{max} (mmol/g)	0.4365	0.3192
	K_L (L/mmol)	6.5274	0.7485
Freundlich model	R^2	0.7932	0.9943
	n	0.2561	1.0614
	K_F (L/mmol)	0.2127	0.1851

Data obtained by isotherm modelling (Figure 8 and Table 3) indicate that the retention of Pb(II) and Hg(II) ions on the clay material is better described by the Freundlich isotherm model compared to the Langmuir isotherm model, which suggests that the retention of metal ions takes place in multiple layers on the adsorbent surface [33]. If in case of Pb(II) ions, the retention process is favourable even at high initial metal ion concentrations (since n is much smaller than 1 [32], Table 3), in case of Hg(II) ions, the spontaneity of the retention process is moderate (n is close to unity-Table 3). All these observations sustain the hypothesis presented above, namely that the retention of Pb(II) and Hg(II) ions from aqueous solutions on clay material involves two processes, one of adsorption and the other of precipitation, whose succession depends on the speciation form of the metal ion, at *p*H values higher than 7.0. Therefore, the improvement of the adsorptive performances of the studied clay material can be done by an acid treatment of it, before being used in the adsorption processes. In this way, the surface alkalinity of the clay material will be reduced and the precipitation processes of metal ions will be limited.

4. Conclusions

In this study, a local natural clay material was used for the efficient removal of Pb(II) and Hg(II) ions from aqueous solution. The adsorption experiments performed in batch systems indicated that the highest adsorption efficiency of the clay material is obtained at initial solution *p*H of 7.0 in case of Pb(II) ions and 2.0 in case of Hg(II) ions, an adsorbent dosage of 4.0 g/L and a contact time of at least 10 min. Under these conditions, the values of removal percents are higher than 97 % in case of Pb(II) and only 55 % in case of Hg(II). This difference in the adsorption behaviour of these two ions is mainly caused by the alkaline characteristics of the clay material ($pH_f > 7.0$), which makes that in the retention processes, in addition to adsorption, precipitation of heavy metal ions has an important role. The modelling of experimental data showed that the adsorption processes followed the Freundlich isotherm model and pseudo-second order kinetic model. Therefore, the retention of Pb(II) and Hg(II) ions on clay material involves two processes, one of adsorption and the other of precipitation, and the succession of these processes depends on the speciation form of the metal ion in aqueous solution.

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