Pol. J. Environ. Stud. Vol. 22, No. 2 (2013), 457-464

Original Research

Adsorption of Pb^{2+} and Cu^{2+} Ions from Aqueous Solutions on Natural Bentonite

Zuzana Melichová*, Ladislav Hromada

Department of Chemistry, Faculty of Natural Sciences, Matej Bel University,
Tajovského 40, 97401 Banská Bystrica, Slovakia

Received: 4 June 2012
Accepted: 9 October 2012

Abstract

The adsorptive properties of natural bentonite from Lieskovec (Slovakia) for the removal of Pb^{2+} and Cu^{2+} ions from aqueous solutions were studied in a batch adsorption system. It was found that the amount of adsorption of metal ion increased with the initial solution pH, metal ion concentration, and contact time, but decreased with the amount of adsorbent. The experimental data were analyzed by both the Freundlich and Langmuir isotherms. The maximum adsorption capacity of the adsorbent for Pb^{2+} and Cu^{2+} ions was calculated from the Langmuir isotherm and found to be 32.68 and 11.34 $mg \cdot g^{-1}$, respectively. The kinetic adsorption experimental results were analyzed using pseudo-first order and pseudo-second order kinetic models. The adsorption kinetic was found to follow a pseudo-second order kinetic model.

Keywords: adsorption isotherm, bentonite, lead, copper

Introduction

Heavy metal pollution is a serious problem for the environment. Heavy metals such as Pb, Cr, Cu, Zn, Sb, Hg, and Cd. are toxic inorganic pollutants in surface and ground water and, by their properties, threaten all living organisms and humans. Some metal ions are toxic even if their concentration is very low, and their toxicity increases with accumulation in water and soils [1].

Lead is one of the most toxic heavy metals [2]. It is widely used in many important industrial applications such as storage battery manufacturing, printing, pigments, fuels, photographic materials, and explosives manufacturing. The toxicity of lead to humans is well-known; it replaces calcium and, consequently, can accumulate in the skeletal system [3]. Exposure to lead is associated with a wide range of effects, including various neurodevelopmental effects, mortality (mainly due to cardiovascular diseases), impaired renal function, hypertension, impaired fertility, and adverse pregnancy outcomes [4].

Although in small concentrations copper is essential to life, excessive levels may be detrimental. Copper also is highly toxic to aquatic organisms. The main sources of copper ions in surface water are, essentially, the industrial waste streams of metal cleaning and plating baths, pulp, paper, paperboard, and wood preservative-employing mills, the fertilizer industry, etc. [5].

Traditional technologies for the removal of heavy metals from water and wastewater include precipitation, ion exchange, adsorption, coagulation, electrolysis, extraction membrane separation, and reverse osmosis [6-8]. However, most of these methods may be extremely expensive or ineffective when the metals are dissolved in large volumes of a solution at a relatively low concentration [9]. Adsorption is very often used for wastewater treatment because it is financially less costly. The main properties of these adsorbents are strong affinity and high loading capacity. Activated carbon and ion exchange resins have been commonly used as adsorbents for the removal of heavy metals from water and wastewater [10]. Inexpensive, readily available and effective materials can be used in place of activated carbon or ion exchange resins for the removal of heavy

---

*e-mail: zuzana.melichova@umb.sk

metals from aqueous solution. A wide range of low-cost sorbents has been studied [11].

Clays have typical properties (large surface area, high cation exchange capacity, chemical and mechanical stability, and a layered structure) that predispose them to be good adsorbents. Bentonite belongs to the group of clay minerals. The main constituent of bentonite is montmorillonite, composed of units made up of two silica tetrahedral sheets with a central alumina octahedral sheet. The isomorphous substitution in tetrahedral and octahedral sheets results in a net negative surface charge on the clay. The resulting negative charge is balanced by hydrated exchangeable cations (e.g. H^+, Na^+, and Ca^{2+}) adsorbed between the layers and around their edges [12]. A number of studies have been reported using clays, mainly montmorillonite, and have shown their effectiveness for the removal of metal ions such as Pb^{2+} [13-20] and Cu^{2+} ions from aqueous solution [21-26].

Bentonite from Lieskovec, used as an adsorbent in this study, is a soft, plastic, and porous rock. It has been shown by previous X-ray analysis on this clay [27] that the dominant component is montmorillonite. The remaining components are quartz, mica, feldspars, kaolinite, and cristobalite. The mineralogical composition [28] and the chemical composition [29] of this material were previously characterized by Andrejkovičová. The total Fe_2O_3 content (5-9%) is higher than in most other Slovak bentonites [30]. The geotechnical properties also were examined [31]. The sorption properties of natural Slovak bentonites (including bentonite from Lieskovec) suitable for application in high-level radioactive waste repositories were compared [32-36]. These results support a more extensive application of natural bentonites in environmental protection.

The adsorption heavy metals on bentonite from Lieskovec under different conditions also was studied [37], but systematic investigation of Pb^{2+} and Cu^{2+} ion sorption on this material has not yet been performed. The objectives of this study were, therefore, to investigate:

(1) the sorption (removal) properties of bentonite from Lieskovec for Pb^{2+} and Cu^{2+} ions, including removal efficiency, sorption isotherms, the effect of initial solution pH, adsorbent dosage, initial metal concentration, and contact time

(2) the kinetics of Pb^{2+} and Cu^{2+} ion sorption onto bentonite.

Materials and Methods

Bentonite in powdered form was obtained from the Lieskovec deposit (near Zvolen, Central Slovakia). This deposit is currently mined by Envigeo Inc., Slovakia. The sample of bentonite was used without further purification. The sample was dry-sieved under open laboratory conditions using a standard mesh (< 200 μm) sieve and dried in a Petri dish in a drying oven at 105ºC for approximately 2-3 h. Then, it was placed in a small polypropylene container and set aside in a desiccator, where it was stored until the next use.

The aqueous solutions of copper ($CuSO_4{\cdot}5H_2O$, Mikro Chem, Slovak Republic) and lead ($Pb(NO_3)_2$, Mikro Chem, Slovak Republic) used in all experiments were prepared with water deionized by reverse osmosis (Demiwa, Watek Czech Republic). The chemicals were of analytical reagent grade. The pH values of the solutions were adjusted by the addition of 0.1 $mol{\cdot}dm^{-3}$ HNO_3 (Analytika, Czech Republic) or 0.1 $mol{\cdot}dm^{-3}$ NaOH (Mikro Chem, Slovak Republic).

Surface Area

The surface area (S) was estimated according to the Sears method [38]. A sample of bentonite (0.5 g) was acidified with 0.1 $mol{\cdot}dm^{-3}$ HCl to a pH 3-3.5. The volume was made up to 50 cm^3 with distilled water after the addition of 10.0 g of NaCl. The titration was carried out with standard 0.1 $mol{\cdot}dm^{-3}$ NaOH to pH 4.0, and then to pH 9.0. The volume (V) required to raise the pH from 4.0 to 9.0 was noted and the surface area was computed from the following equation:

$$S\,(m^2{\cdot}g^{-1}) = 32\,V - 25 \qquad (1)$$

According to the procedure described above, the surface area was determined to be 57.4 $m^2{\cdot}g^{-1}$ bentonite.

Cation Exchange Capacity

Cation exchange capacity (CEC) was determined by the ammonium acetate method [29]. A sample of bentonite (0.5 g) and 200 cm^3 of 1 $mol{\cdot}dm^{-3}$ ammonium acetate were mixed in a polyethylene tube. After 24 hours, the sample was washed with ethanol, filtered and dried, then put in a distillation bank with 2 g of MgO and 200 cm^3 of deionized water. Subsequently, 100 cm^3 of distillate was placed in a flask containing 5 cm^3 of 4% boric acid and five drops of bromcresol green, and titrated with 0.1 $mol{\cdot}dm^{-3}$ HCl. The amount of HCl was then taken to calculate the CEC.

The CEC was measured as 40.53 $mmol{\cdot}100\ g^{-1}$ bentonite, in agreement with the reported value [27].

Adsorption Experiments

The ability of bentonite to adsorb metal ions from aqueous solution was studied under various optimized conditions of pH, adsorbent dosage, concentration of metals, and contact time.

Batch adsorption experiments were carried out at 20ºC in 250 cm^3 Erlenmeyer flasks by mixing 0.5 g of the adsorbent with 100 cm^3 of a solution of lead (Pb^{2+}) or copper (Cu^{2+}). The initial pH of the solutions was adjusted with HNO_3 or NaOH to the desired value. The pH values of all solutions were measured by a Model 340 pH meter (WTW, Germany). After 120 min, the suspensions were centrifuged and the solutions were analyzed for metal ions by atomic absorption spectrometry (AAS). The concentrations of the metal ions before and after adsorption were determined using an AVANTA Σ atomic adsorption spectrometer (GBC Scientific, Australia) with acetylene-air flame atomization. The data were processed by the GBC Avanta software. The working wavelengths for Pb^{2+} ions were 283.3 nm (to 50 $mg \cdot dm^{-3}$) and 261.4 nm (to 500 $mg \cdot dm^{-3}$), and for Cu^{2+} ions 222.6 nm (to 50 $mg \cdot dm^{-3}$) and 249.2 nm (to 500 $mg \cdot dm^{-3}$). The instrument response was periodically checked by using standard metal solutions. All experiments were repeatedly performed in duplicate. The experimental error limit of duplicates was maintained at ±5%.

The effect of contact time was observed by mixing 5 g of the adsorbent with 1000 cm^3 of a solution of Cu^{2+} or Pb^{2+} ions. The suspension was stirred and, at regular time intervals, 2 cm^3 of solution were collected, centrifuged, and then analyzed for metal ions by AAS. The concentrations of the metal ions before adsorption also were measured.

The amount of adsorbed metal ions per mass unit of sorbent at time q_t ($mg \cdot g^{-1}$) was calculated by the following equation:

$$q_t = \frac{(c_o - c_t)V}{m} \tag{2}$$

...where c_o is the initial concentration of metal ions ($mg \cdot dm^{-3}$), c_t is the concentration of metal ions left in aqueous solutions at time t ($mg \cdot dm^{-3}$), V is the volume of the aqueous phase (dm^3), and m is the amount of the bentonite (g).

The adsorption percentage (*Ads.%*) was calculated by the following expression:

$$Ads.(\%) = \frac{c_o - c_t}{c_o} 100 \tag{3}$$

Results and Discussion

Effect of pH

The effect of the pH of the solution is an important controlling parameter in the adsorption processes. In the present work, the adsorption of Pb^{2+} and Cu^{2+} ions on bentonite was studied at different pH levels ranging from 2.0 to 9.0 at a constant clay amount of 5 $g \cdot dm^{-3}$. The initial concentration of metal ions was 50 $mg \cdot dm^{-3}$. As seen in Fig. 1, Pb^{2+} and Cu^{2+} adsorption by bentonite increased when the initial pH of the solution was increased from 2 to 4 for Pb and from 2 to 7 for Cu, respectively, and then reached a plateau at pH > 4 and pH > 7. This phenomenon was consistent with previous studies [15].

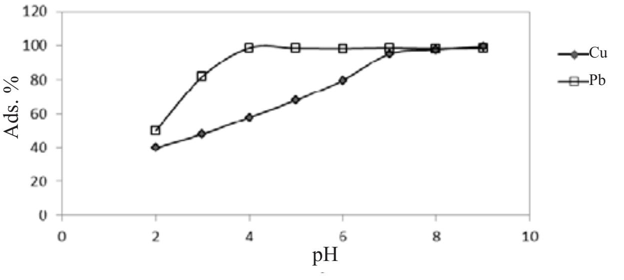

Fig. 1. Effect of pH on the adsorption of Pb^{2+} and Cu^{2+} ions (experimental conditions: 0.5 g adsorbent, 100 cm^3 solution, c_o Cu^{2+} or Pb^{2+} 50 $mg \cdot dm^{-3}$, temperature 20ºC).

The lowest metal ions sorption rates were obtained at pH 2, which may be caused by the competitive influence of H^+ ions and the presence of a relatively small number of available sites in the disturbed structure of bentonite. The aluminol and silanol groups on the bentonite surface are more protonated and, hence, they are less available to retain the investigated metals. H^+ ions compete with the metal ions for the adsorptive sites in the system, resulting in reduced sorption for metal ions. The metal ions were completely released under extreme acidic conditions [39].

As pH increased, exchangeable ions (i.e. Na^+, K^+, Ca^{2+}, and Mg^{2+}, present at the exchangeable sites of bentonite) were exchanged for Pb^{2+} and Cu^{2+} ions, respectively, in the aqueous solutions. The basic mechanism that governs the adsorption characteristics of bentonite are adsorption and ion exchange. However, at pH values higher than 5 for Pb and 7 for Cu, metal ions were transformed to poorly soluble hydroxides, which precipitated such that the aqueous concentrations were below the detection limit.

Generally, clay can adsorb metals ions via two different mechanisms:

(1) at low pH values, the dominating process is cation exchange in the interlayers, resulting from the interactions between ions and negative permanent charge
(2) at high pH values, the uptake of metal ions is accompanied by the release of hydrogen ions, and seems to be more specific than uptake at low pH values (formation of inner-sphere complexes through Si–O− and Al–O− groups at the clay particle edges) [41].

Effect of Adsorbent Dosage

The effect of adsorbent dosage on the adsorption of Pb^{2+} and Cu^{2+} ions was studied at different dosages in the solution at pH 5. As shown in Fig. 2, the adsorption percentage of removed Pb^{2+} and Cu^{2+} ions increased as the dosage of bentonite increased from 1.0 to 10.0 $g \cdot dm^{-3}$. This may be explained by the metal ions competing for limiting adsorption sites at a lower bentonite dosage. The increase in the adsorption percentage with an increase in adsorbent dosage

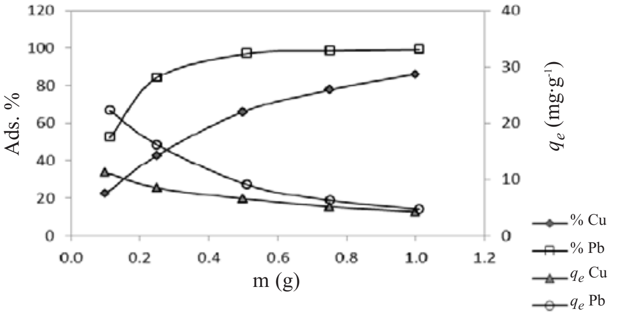

Fig. 2. Effect of the dosage of bentonite on the adsorption of Pb^{2+} and Cu^{2+} ions (experimental conditions: 100 cm^3 solution, c_o Cu^{2+} or Pb^{2+} 50 $mg \cdot dm^{-3}$, pH 5, temperature 20ºC).

was due to an increase in active sites on the adsorbent, thus facilitating the penetration of metal ions to the sorption sites [42]. The adsorption percentage of Pb^{2+} was greater than that of Cu^{2+} ions. However, the adsorption capacity of Pb^{2+} and Cu^{2+} ions was observed to decrease with an increase in adsorbent dosage. These observations are in agreement with others reported in the literature for the adsorption of metals ions by different materials [7, 18, 21, 23]. The adsorbent dosage mass was fixed at 5 g·dm^{-3} for further equilibrium and kinetic studies.

Effect of Initial Metal Concentration

The effect of the initial concentration of Pb^{2+} and Cu^{2+} ions was studied at different metal concentrations in the solution at pH 5, with a constant amount of bentonite (5 g·dm^{-3}).

From Fig. 3, it can be seen that the equilibrium adsorption capacity of the bentonite, q_e, increased with an increased initial Cu^{2+} and Pb^{2+} concentration, while the percentage removal showed the opposite trend. When the initial concentration of Pb^{2+} ions increased from 50 to 500 mg·dm^{-3}, the adsorption capacity of bentonite increased from 8.32 to 29.77 mg·g^{-1} and the percentage removal decreased from 83.06% to 31.62%. With the increased concentration of Cu^{2+} ions, the adsorption capacity of bentonite increased from 6.70 to 10.74 mg·g^{-1} and the percentage removal decreased from 74.28% to 21.81%. A similar observation was reported previously [38].

Adsorption Isotherms

Adsorption isotherms are important for research into an adsorption process. Numerous isotherm equations have been reported, and two major isotherms, the Freundlich and Langmuir isotherms, were applied to establish the relationship between the amount of Pb^{2+} and Cu^{2+} ions adsorbed by bentonite and their equilibrium concentrations in aqueous solution.

The Freundlich isotherm is given as:

$$q_e = K_F \, c_e^{\frac{1}{n}} \tag{4}$$

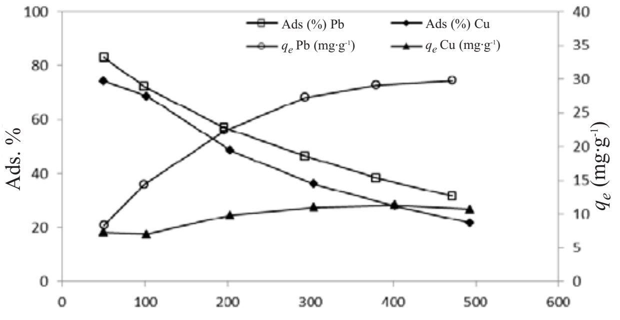

Fig. 3. Effect of the initial metal concentration on the adsorption of Pb^{2+} and Cu^{2+} ions (experimental conditions: 100 cm^3 solution, 0.5 g bentonite, pH 5, temperature 20ºC).

The linear form is given by:

$$\log q_e = \log K_F + \frac{1}{n} \log c_e \tag{5}$$

...where c_e and q_e are the equilibrium concentrations of metal ions in the liquid phase and in the solid phase, respectively (mg·dm-^{3}), K_F is the surface adsorption equilibrium constant (mg·g-^{1}), and n is an empirical parameter related to the intensity of adsorption, which varies with the heterogeneity of the adsorbent. For values in the range 0.1 < 1/n < 1, adsorption is favorable.

The Freundlich isotherm is valid for heterogeneous surfaces and predicts an increase in the concentration of the ionic species adsorbed onto the surface of the solid when the concentration of said species in the liquid phase is increased [17, 43].

The Langmuir adsorption isotherm, which is valid for monolayer sorption onto a surface with a finite number of identical sites, can be expressed as:

$$q_e = \frac{q_m \, b \, c_e}{1 + b \, c_e} \tag{6}$$

...where c_e is the equilibrium concentration of adsorbate in the solution (mg·dm^{-3}), q_e is the amount of metal ions adsorbed per unit weight of the sorbent at equilibrium concentration (mg·g^{-1}), q_m the maximum adsorption at monolayer coverage (mg·g^{-1}), and b is the Langmuir constant related to the affinity of binding sites (dm^3·mg^{-1}).

The linear form of the equation can be written as:

$$\frac{c_e}{q_e} = \frac{1}{b \, q_m} + \frac{1}{q_m} c_e \tag{7}$$

The adsorption isotherms were determined at pH 5 for a concentration range of 50-500 mg·dm^{-3}. All solutions contained a fixed mass of bentonite (5 g of bentonite per 1 dm^3 of solution). The experimental data were plotted as logq_e versus logc_e and c_e/q_e versus c_e respectively and are shown in Figs. 4 and 5. The constants K_f and n were calculated from Eq. (5) and Freundlich plots (Fig. 4). The values of q_m and b were determined from Eq. (7) and Langmuir plots (Fig. 5). The calculated results and correlation coefficients (R^2) are listed in Table 1. Values of the correlation coeffi-

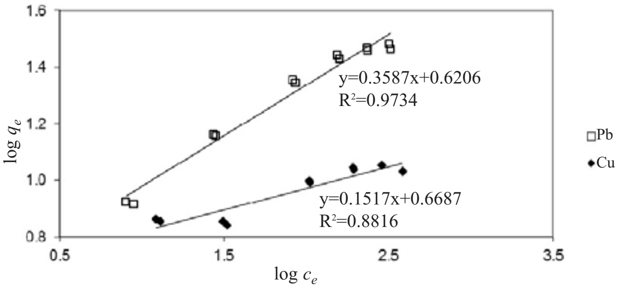

Fig. 4. Freundlich adsorption isotherm.

Table 1. Parameters of the Freundlich and Langmuir isotherms.

Metal	Freundlich			Langmuir		
	K_f	n	R^2	q_m	b	R^2
Cu	4.6602	6.5920	0.8816	11.3379	0.0853	0.9966
Pb	4.1745	2.7878	0.9734	32.6797	0.0313	0.9972

Table 2. Values of maximum sorption capacities of some clay minerals for Pb^{2+} and Cu^{2+} ions.

Sorbent	Cu q_m ($mg \cdot g^{-1}$)	[Ref]	Sorbent	Pb q_m ($mg \cdot g^{-1}$)	[Ref]
Na-bentonite	17.88	[7]	Bentonite	7.56	[11]
Ca-bentonite	12	[21]	Montmorillonite	57.0	[14]
Natural bentonite	7.94	[23]	Montmorillonite	31.06	[15]
Natural bentonite	44.84	[25]	Natural bentonite	107	[18]
Montmorillonite	28.8	[26]	Natural bentonite	71	[19]
Na-bentonite	3.04	[40]	Na-bentonite	9.58	[40]
Natural bentonite	11.34	This study	Natural bentonite	32.68	This study

cients (R^2) show that the Langmuir model fitted best to our experimental data. The values of q_m were found to be 32.68 mg of Pb per gram of bentonite and 11.34 mg of Cu per gram of bentonite, under the optimum adsorption conditions.

Several researchers have studied the adsorption capacity of clay mineral samples. The comparison of the bentonite from Lieskovec with various adsorbents in terms of adsorption capacity for Pb^{2+} and Cu^{2+} ions from aqueous solution at laboratory temperature is given in Table 2. The lower capacity for Cu^{2+} with respect to Pb^{2+} ions depends on the different geometry of its aquation, which has a tetragonal distortion due to the Jahn-Teller effect that makes its introduction into lamellar spaces more difficult.

Kinetic of Adsorption

The pseudo-first order equation of Lagergren [44] is generally expressed as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{8}$$

...where k_1 is the pseudo-first order adsorption rate constant ($dm^3 \cdot min^{-1}$) and q_t and q_e are the amounts of metal ions adsorbed at time t and at equilibrium, respectively ($mg \cdot g^{-1}$).

After integration and applying boundary conditions ($t = 0$ to t and $q_t = 0$ to q_e), the integrated form of equation (8) becomes:

$$ln(q_e - q_t) = ln\, q_e - k_1 t \tag{9}$$

The value of k_1 can be obtained from the slope of the linear plot of $\ln(q_e - q_t)$ versus t.

A pseudo-second order kinetic model proposed by Ho and McKay [45, 46] was used to fit the adsorption kinetic data using the equation:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{10}$$

...where k_2 is the pseudo-second order adsorption rate constant ($g \cdot mg^{-1} \cdot min^{-1}$) and q_t and q_e are the amounts of solute adsorbed per unit adsorbent ($mg \cdot g^{-1}$) at time t and at equilibrium, respectively.

For the boundary conditions ($t = 0$ to t and $q_t = 0$ to q_e), the integrated form of equation (10) becomes:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \tag{11}$$

The plot of t/q_t versus t gives a straight line, which allows the computation of q_e and k_2.

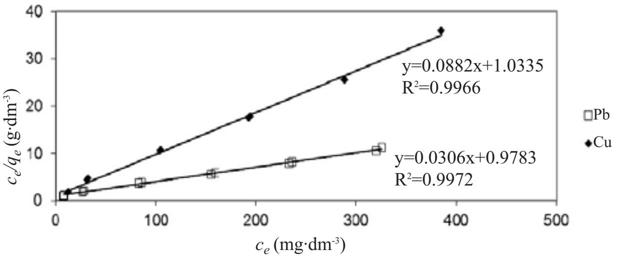

Fig. 5. Langmuir adsorption isotherm.

In this study, the initial lead and copper concentrations were determined as 50, 100, and 200 mg·dm^{-3}. The effects of contact time on the removal efficiency of Pb^{2+} and Cu^{2+} ions using 5 g·dm^{-3} bentonite at pH 5 are shown in Figs. 6 and 7. It can be seen that the adsorbed amounts of metal ions on bentonite increased with an increase in contact time. The adsorption rate of both ions on bentonite reaches equilibrium within 120 min.

Increasing the initial metal ion concentration led to an increase in adsorption capacity, q_t, with various contact times. This may be attributed to the initial concentration, which provides an important driving force to overcome all mass transfer resistances of metal ions between the aqueous and solid phases, hence a higher initial concentration of metal ions will enhance the adsorption process.

A very high adsorption rate was observed at the beginning of the reaction because of the great number of sites available for sorption; adsorption equilibrium was gradually achieved.

In order to calculate the adsorption rate constants of copper and lead, pseudo-first order reaction kinetics and pseudo-second order reaction kinetics were applied to the experimental data. The plots of $\ln(q_e - q_t)$ versus t for the Lagergren pseudo-first order model were not shown as a figure because the R^2 values for this model at studied temperatures were low (0.543-0.858 for Cu^{2+} adsorption and 0.265-0.632 for Pb^{2+} adsorption) (Table 3). The values of q_e were not in agreement with the experimental q_e values. This indicates that the pseudo-first order equation might not be sufficient to describe the interaction between Pb^{2+} and Cu^{2+} ions and bentonite.

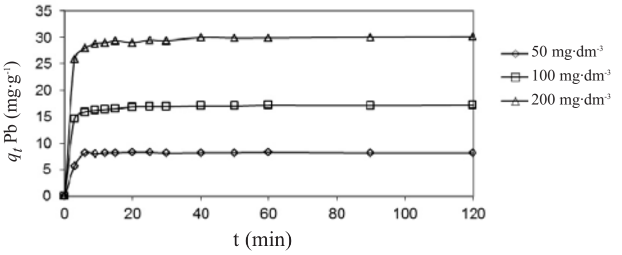

Fig. 6. Effect of time on the adsorption of Pb^{2+} ions for various initial concentrations of Pb^{2+} ions (experimental conditions: 1000 cm^3 solution, 5 g adsorbent, pH 5, temperature 20ºC).

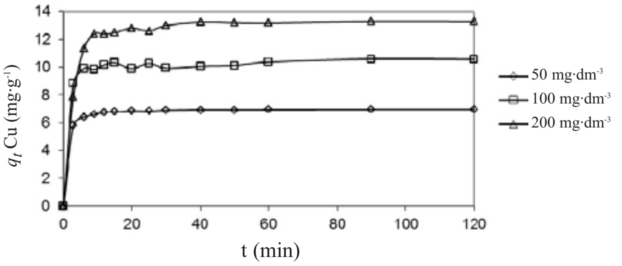

Fig. 7. Effect of time on the adsorption of Cu^{2+} ions for various initial concentrations of Cu^{2+} ions (experimental conditions: 1000 cm^3 solution, 5 g adsorbent, pH 5, temperature 20ºC).

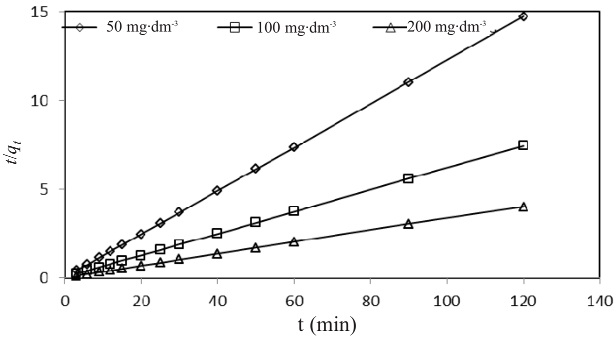

Fig. 8. Pseudo-second order adsorption kinetics of Pb^{2+} ions on bentonite.

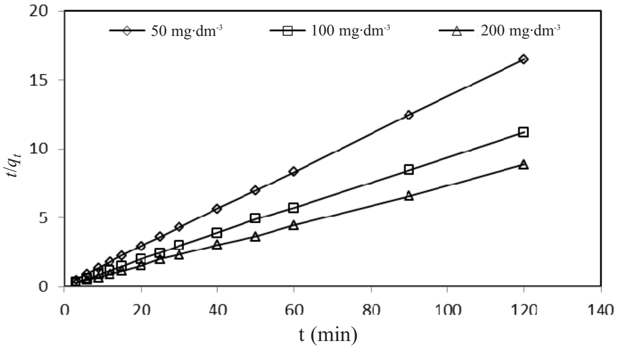

Fig. 9. Pseudo-second order adsorption kinetics of Cu^{2+} ions on bentonite.

Using Eq. (11), t/q_t was plotted versus t at different adsorbent concentrations and the pseudo-second order sorption rate constant k_2 and q_e values were determined from the slopes and intercepts of the plots (Figs. 8 and 9). The values of these parameters are presented in Table 2. The correlation coefficients for the linear plots were high, indicating that the pseudo-second order kinetic model best describes the adsorption of Pb^{2+} and Cu^{2+} ions on bentonite.

The calculated q_e values agreed very well with the experimental data in the case of pseudo-second order kinetics. These results indicate that the sorption process of metal ions onto bentonite followed pseudo-second order kinetics, which meant that external mass transfer and intraparticle diffusion were both involved in the sorption process [19].

From Table 3 it can be seen that the pseudo-second order kinetic rate constants decreased with an increase in the initial Pb^{2+} and Cu^{2+} concentrations. This is due to less competition for active surface sorption sites at a lower concentration. At higher concentrations, competition for the adsorption active sites will be increased and, consequently, the adsorption rate will become slower.

Several authors have also reported the applicability of the pseudo-second order kinetic model for modelling the removal of copper and lead using other sorbents [15, 19].

Many studies have reported that the first-order Lagergren equation does not fit well to the initial stages of the adsorption processes. The first-order kinetic process has been used for reversible reactions with equilibrium being

Table 3. Comparison of adsorption rate constants, experimental and calculated q_e values for the pseudo-first and pseudo-second order reaction kinetics of adsorption of Pb^{2+} and Cu^{2+} ions on bentonite.

Metal	Initial metal concentration ($mg \cdot dm^{-3}$)	q_e, experimental ($mg \cdot g^{-1}$)	Pseudo-first order			Pseudo-second order		
			k_1 ($dm^3 \cdot min^{-1}$)	q_e, calculated ($mg \cdot g^{-1}$)	R^2	k_2 ($g \cdot mg^{-1} \cdot min^{-1}$)	q_e, calculated ($mg \cdot g^{-1}$)	R^2
Pb	50	8.25	-0.017	0.43	0.2648	0.488	8.24	1
	100	16.23	-0.028	1.14	0.6315	0.084	16.30	0.9999
	200	29.96	-0.022	2.52	0.5820	0.043	29.99	0.9999
Cu	50	7.35	-0.022	1.25	0.8193	0.088	7.32	0.9998
	100	10.74	-0.025	1.41	0.8584	0.073	10.89	0.9994
	200	13.72	-0.031	1.68	0.5431	0.062	13.75	0.9992

established between the liquid and solid phases, whereas the second-order kinetic model assumes that the rate-limiting step may be chemical adsorption. In many cases, the second-order equation correlates well in adsorption studies.

Conclusion

The bentonite from Lieskovec can be used as an effective adsorbent for the adsorption of Pb^{2+} and Cu^{2+} ions from aqueous solutions.

The initial pH of the aqueous solution is an important parameter in the adsorption process. The adsorption of metal ions increased with an increase in the pH of the solution. By increasing the adsorbent dosage, the amount of Pb^{2+} and Cu^{2+} ions adsorbed per unit mass of the adsorbent decreased at equilibrium. Raising the initial metal ion concentration led to an increase in Pb^{2+} and Cu^{2+} uptake by bentonite. The experimental data were fitted better to the Langmuir than to the Freundlich isotherm. The greatest adsorption capacity of Lieskovec bentonite for Pb^{2+} and Cu^{2+} ions was 32.7 and 11.3 $mg \cdot g^{-1}$, respectively.

The adsorption kinetics followed a pseudo-second order kinetic model. The values of the pseudo-second order rate constant for the adsorption of metal ions on bentonite decreased in the order $Pb^{2+} > Cu^{2+}$.

Acknowledgements

Financial support of this work by the Ministry of Education, Science, Research and Sport of the Slovak Republic (project VEGA 2/0065/11) is acknowledged.

References

1. PITTER P. Hydrochemie. Vydavatelsví VŠCHT, Praha, **2009** [In Czech].
2. NORDBERG G.F., FOWLER B.A., NORDBERG M., FRIBERG L.T. (Eds.) Handbook on the Toxicology of Metals (Third Edition), Elsevier, Amsterdam, **2007**.
3. ANIELAK A.M., SCHMIDT R. Sorption of Lead and Cadmium Cations on Natural and Manganese-Modified Zeolite. Pol. J. Environ. Stud. **20**, (1), 43, **2011**.
4. WHO, Guidelines for drinking-water quality - 4th ed., WHO Press, Geneva, **2011**.
5. STYLIANOU M.A., INGLEZAKIS V.J., MOUSTAKAS K.G., MALAMIS S.PH., LOIZIDOU M.D. Removal of Cu(II) in fixed bed and batch reactors using natural zeolite and exfoliated vermiculite as adsorbents. Desalination **215**, 133, **2007**.
6. FU F., WANG Q. Removal of heavy metal ions from wastewater: A review. J. Environ. Manage. **92**, 407, **2011**.
7. ZHI-RONG L., SHAO-QI Z. Adsorption of copper and nickel on Na-bentonite. Process Saf. Environ. Prot. **88**, 62, **2010**.
8. VINODH R., PADMAVATHI R., SANGEETHA D. Separation of heavy metals from water samples using anion exchange polymers by adsorption process. Desalination **267**, 267, **2011**.
9. BULUT Y., TEZ Z. Removal of heavy metals from aqueous solution by sawdust adsorption, J. Environ. Sci. **19**, 160, **2007**.
10. KADIRVELU K., THAMARAISELVI K., NAMASIVAYAM C. Removal of Heavy Metal from Industrial Wastewaters by Adsorption onto Activated Carbon Prepared from an Agricultural Solid Waste. Bioresource Technol. **76**, 63, **2001**.
11. BAILEY S.E., OLIN T.J., BRICKA R.M., ADRIAN D.D. A review of potentially low-cost sorbents for heavy metals. Water Res. **33**, 2469, **1999**.
12. ŠUCHA V. Íly v geologických procesoch. Acta Geologica, Universitas Comenianae: Monografická séria, Bratislava, **2001** [In Slovak].
13. AYARI F., SRASRA E., TRABELSI-AYADI M. Retention of lead from an aqueous solution by use of bentonite as adsorbent for reducing leaching from industrial effluents. Desalination **206**, 270, **2007**.
14. ZHANG S.Q., HOU W.G. Adsorption behavior of Pb(II) on montmorillonite. Colloids Surf. A, **320**, 92, **2008**.
15. BHATTACHARYYA K.G., GUPTA S.S. Pb(II) uptake by kaolinite and montmorillonite in aqueous medium: Influence of acid activation of the clays. Colloids Surf. A **277**, 191, **2006**.
16. DONAT R., AKDOGAN A., ERDEM E., CETISLI H. Thermodynamics of Pb^{2+} and Ni^{2+} adsorption onto natural bentonite from aqueous solutions. J. Colloid Interface Sci. **286**, 43, **2005**.

17. MISHRA P.C., PATEL R.K. Removal of lead and zinc ions from water by low cost adsorbents. J. Hazard. Mater. **168**, 319, **2009**.
18. HEFNE J.A., MEKHEMER W.K., ALANDIS N.M., ALDAYEL O.A., ALAJYAN T. Kinetic and thermodynamic study of the adsorption of Pb(II) from aqueous solution to the natural and treated bentonite. Int. J. Phys. Sci. **3**, (11), 281, **2008**.
19. HAMIDPOUR M., KALBASI M., AFYUNI M., SHARIATMADARI H., FURRER G. Sorption of lead on Iranian bentonite and zeolite: kinetics and isotherms. Environ. Earth Sci. **62**, 559, **2011**.
20. INGLEZAKIS V.J., STYLIANOU M.A., GKANTZOU D., LOIZIDOU M.D. Removal of Pb(II) from aqueous solutions by using clinoptilolite and bentonite as adsorbents. Desalination **210**, 248, **2007**.
21. DING S.L., SUN Y.Z., YANG C.N., XU B.H. Removal of copper from aqueous solutions by bentonites and the factors affecting it. Min. Sci. Technol. B, 0489, **2009**.
22. EREN E., AFSIN B. An investigation of Cu(II) adsorption by raw and acid-activated bentonite: A combined potentiometric, thermodynamic, XRD, IR, DTA study. J. Hazard. Mater. **151**, 682, **2008**.
23. KARAPINAR N., DONAT R. Adsorption behaviour of Cu^{2+} and Cd^{2+} onto natural bentonite. Desalination **249**, 123, **2009**.
24. AL-QUNAIBIT M.H., MEKHEMER W.K., ZAGHLOUL A.A. The adsorption of Cu(II) ions on bentonite - a kinetic study. J. Colloid Interface Sci. **283**, 316, **2005**.
25. VELI S., ALYÜZ B. Adsorption of copper and zinc from aqueous solutions by using natural clay. J. Hazard. Mater. **149**, 226, **2007**.
26. BHATTACHARYYA K.G., GUPTA S.S. Kaolinite, montmorillonite, and their modified derivatives as adsorbents for removal of Cu(II) from aqueous solution. Sep. Purif. Technol. **50**, 388, **2006**.
27. BRTÁŇOVÁ A., MELICHOVÁ Z., KOMADEL P. Sorption of Cu^{2+} from aqueous solutions by Slovak bentonites. Ceram.-Silik. **56**, (1), 55, **2012**.
28. ANDREJKOVIČOVÁ S., PENTRÁK M., JANKOVIČ Ľ., KOMADEL P. Sorption of heavy metal cations on rhyolitic and andesitic bentonites from Central Slovakia. Geol. Carpath. **61**, 163, **2010**.
29. ANDREJKOVIČOVÁ S., MADEJOVÁ J., CZÍMEROVÁ A., GALKO I., DOHRMANN R., KOMADEL P. Mineralogy and chemistry of Fe-rich bentonite from Lieskovec deposit (Central Slovakia). Geol. Carpath. **57**, 371, **2006**.
30. KOMADEL P., ANASTÁCIO A.S., ANDREJKOVIČOVÁ S. STUCKI J.W. Iron phases identified in bentonite from the Lieskovec deposit (Slovakia) by variable-temperature Mossbauer spectroscopy. Clay Miner. **43**, 1, **2008**.
31. ANDREJKOVIČOVÁ S., JANOTKA I., KOMADEL P. Evaluation of geotechnical properties of bentonite from Lieskovec deposit, Slovakia. Appl. Clay Sci. **38**, 297, **2008**.
32. GALAMBOŠ M., KUFČÁKOVÁ J., RAJEC P. Sorption of strontium on Slovak bentonites. J. Radioanal. Nucl. Chem. **281**, (3), 347, **2009**.
33. GALAMBOŠ M., KUFČÁKOVÁ J., RAJEC P. Adsorption of cesium on domestic bentonites. J. Radioanal. Nucl. Chem. **281**, (3), 485, **2009**.
34. GALAMBOŠ M., KUFČÁKOVÁ J., ROSSKOPFOVÁ O., RAJEC P. Adsorption of cesium and strontium on natrified bentonites. J. Radioanal. Nucl. Chem. **283**, (3) 803, **2010**.
35. GALAMBOŠ M., PAUČOVÁ V., KUFČÁKOVÁ J., ROSSKOPFOVÁ O., RAJEC P., ADAMCOVÁ R. Cesium sorption on Bentonites and Montmorillonite K10. J. Radioanal. Nucl. Chem. **284**, 55, **2010**.
36. GALAMBOŠ M., DAŇO M., ROSSKOPFOVÁ O., ŠERŠEŇ F., KUFČÁKOVÁ J., ADAMCOVÁ R., RAJEC, P. Effect of gamma-irradiation on adsorption properties of Slovak bentonites. J. Radioanal. Nucl. Chem. **292**, (2), 481, **2012**.
37. ANDREJKOVIČOVÁ S., PENTRÁK M., JANKOVIČ L., KOMADEL P. Sorption of heavy metal cations on rhyolitic and andesitic bentonites from Central Slovakia. Geol. Carpath. **61**, (2), 163, **2010**.
38. SEARS G.W. Determination of Specific Surface Area of Colloidal Silica by Titration with Sodium Hydroxide. Anal. Chem. **28**, 1981, **1956**.
39. ABDEL-GHANI N.T., HEFNY M., EL-CHAGHABY G.A.F. Removal of lead from aqueous solution using low cost abundantly available adsorbents. Int. J. Environ. Sci. Technol. **4**, (1), 67, **2007**.
40. ABOLLINO O., ACETO M., MALANDRINO M., SARZANINI C., MENTASTI E. Adsorption of heavy metals on Na-montmorillonite. Effect of pH and organic substances. Water Res. **37**, 1619, **2003**.
41. KRAEPIEL A.M.L., KELLER K., MOREL F.M.M. A model for metal adsorption on montmorillonite. J. Colloid Interface Sci. **210**, 43, **1999**.
42. SARI A., TUZEN M., CITAK D., SOYLAK M. Adsorption characteristics of Cu(II) and Pb(II) onto expanded perlite from aqueous solution, J. Hazard. Mater. **148**, 387, **2007**.
43. FERNÁNDEZ-NAVA Y., ULMANU M., ANGER I., MARAÑÓN E., CASTRILLÓN L. Use of Granular Bentonite in the Removal of Mercury (II), Cadmium (II) and Lead (II) from Aqueous Solutions. Water Air Soil Pollut. **215**, 239, **2011**.
44. LAGERGREN S. Zur theorie der sogenannten adsorption gelöster stoffe. Kungliga Svenska Vetenskapsakademiens. Handlingar **24**, (4), 1, **1898**.
45. HO Y.S., McKAY G. Pseudo-second order model for sorption processes, Process Biochem. **34**, 451, **1999**.
46. HO Y.S. Isotherms for the sorption of lead onto peat: Comparison of linear and non-linear methods. Pol. J. Environ. Stud. **15**, (1), 81, **2006**.