



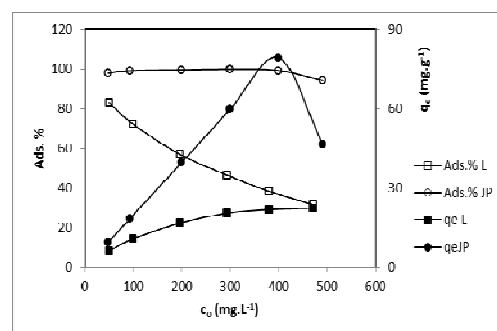
REMOVAL OF Pb^{2+} IONS FROM AQUEOUS SOLUTIONS BY SLOVAK BENTONITES

Zuzana MELICHOVÁ,* Ladislav HROMADA and Andrea LUPTÁKOVÁ

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

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The adsorptive properties of Slovak bentonites from deposits Jelšovský Potok and Lieskovec for the removal of Pb^{2+} ions from aqueous solutions were studied in a batch adsorption system at room temperature. The effect of pH, initial concentration of Pb^{2+} ions, contact time and amount of bentonite were investigated. It was found that the amount of adsorption of metal ion increased with the initial solution pH, metal ion concentration and contact time, but was decreased with the amount of adsorbent. The equilibrium adsorption capacity of the adsorbents used for Pb^{2+} ions was extrapolated using the linear Freundlich and Langmuir adsorption isotherms. The experimental data measured for both bentonites were fitted better to the Langmuir isotherm from which the maximum adsorption capacity was calculated. By comparing the measured results for both bentonites it is evident that the bentonite from Jelšovský Potok is more suitable for sorption of lead.



INTRODUCTION

Lead (Pb) is one of the major environmental pollutants. It is not biodegradable metal and it is toxic to humans.¹ It tends to accumulate in living organisms and causes various diseases and disorders. It replaces calcium and, consequently, can accumulate in the bone system.² Lead can enter and be adsorbed into the human body through inhalation or with skin contact and can produce adverse effects on virtually every system in the body. Low levels of Pb^{2+} have been identified with anemia while high levels cause severe dysfunction of the kidneys, liver, the central and peripheral nervous system, the reproductive system, and high blood pressure.³ Slovak legislation (in accordance with EU legislation) and the WHO recommended maximum limit in drinking water $10 \mu\text{g}\cdot\text{L}^{-1}$ of total Pb .⁴

Lead is used principally in the production of lead-acid batteries, solder and other alloys. The organolead compounds tetraethyl and tetramethyl lead have also been used extensively as antiknock and lubricating agents in petrol, although their use for these purposes has largely been phased out in many countries. Lead may enter the environment during its mining, ore processing, smelting, refining use, recycling or disposal. Due to toxic effects of lead and other toxic metal ions, their removal from water and wastewater is important in terms of protection of public health and environment.⁵

Heavy metals in water are removed by processes such as chemical precipitation, ion exchange, solvent extraction, reverse osmosis and electroflotation. The disadvantage of many of these methods is the high cost, the need for continuous feeding of chemicals, and production of toxic

* Corresponding author: Zuzana.Melichova@umb.sk

sludge. Adsorption at a solid solution interface is very often used for wastewater treatment, because it is financially affordable. The main properties of the adsorbents for heavy metal removal are strong affinity and high loading capacity. In recent years, various conventional and non-conventional adsorbents, such as activated carbon,⁶ natural and synthetic zeolites^{2,7,8} and bentonites,⁹⁻¹² montmorillonite,¹³⁻¹⁶ blast furnace slag and fly ash,¹⁷ expanded perlite,¹⁸ sawdust,^{19,20} agricultural byproducts^{21,22} etc. have been used as adsorbents for the removal of lead from water and wastewater.

Clay minerals are used as a major group of inorganic natural substances. They constitute an essential component of many different rocks, soil and river sediments in nature. Exceptional properties (high specific surface, ion exchange capacity, sorptive and catalytic properties) predispose them to practical use in many technological and environmental applications. Clay minerals are known to have a typical layered structure which consists of layers of tetrahedron (SiO_4)⁴⁻ and octahedron $[\text{Al}(\text{OH})_6]^{3-}$ or $[\text{Mg}(\text{OH})_6]^{4-}$. Between the layers there is interlaminar space, which can include fixed cations. In some cases they are hydrated and replaceable.

Montmorillonites (dioctahedral smectites) are one of the major groups of clay minerals in terms of environmental applications. They dominated in clay mineralogical rock bentonite; mined and exploited in Slovakia, too. In Slovakia, there are bentonites of different geological origin, which significantly affects composition of clays (eg. type of bearing rhyolite is deposit Jelšový Potok in Kremnické vrchy, bearing andesite type eg. Lieskovec in Zvolenská kotlina).²³ The sorption properties of natural Slovak bentonites suitable for application in high-level radioactive waste repositories were compared.²⁴⁻²⁸ Sorption properties decreased in the order Jelšový Potok > Kopernica > Lieskovec > Lastovce > Dolná Ves. These results support more extensive application of natural bentonites in environmental protection.

Bentonites from Lieskovec (**L**) and Jelšový Potok (**JP**), used as adsorbents in this study, are a soft, plastic and porous rock. It has been shown by previous X-ray analysis on these clays²⁹ that the dominant component is montmorillonite. The remaining components are quartz, mica, feldspars, kaolinite and cristobalite. The mineralogical composition³⁰ and the chemical composition³¹ of these materials were previously characterised by Andrejkovičová. The total Fe_2O_3 content (5-9%) in **L** is higher than in most other Slovak bentonites.³²

Geotechnical properties of **L** were also examined.³³ The adsorption of heavy metals on these adsorbents under different conditions was also studied,^{29,30,34} but systematic investigation of Pb^{2+} ions sorption has not yet been performed.

The objectives of this study were to investigate the effect of initial solution pH, adsorbent dosage, initial metal concentration and contact time on the adsorption of Pb^{2+} on industrial products from Slovak bentonites, determine their adsorption efficiency and compare their sorption properties.

EXPERIMENTAL

Two industrial products made from two Slovak bentonites Jelšový Potok (**JP**) and Lieskovec (**L**) were provided by the Envigeo, Ltd, Slovakia. The samples of bentonites were used without further purification. The samples were dry-sieved under open laboratory conditions using a standard mesh (< 200 μm) sieve and dried in a Petri dish in a drying oven at a temperature of 105°C for approximately 2-3 h. Then, they were placed in small polypropylene containers and stored in a desiccator prior to next use.

All used chemicals were of analytical reagent grade. Stock solution of Pb^{2+} was prepared by dissolving $\text{Pb}(\text{NO}_3)_2$ (Mikro Chem, Slovak Republic). Water deionised by reverse osmosis (Demiwa, Watek Czech Republic) was used for the treatments. The pH values of the solutions were adjusted by the addition of 0.1 $\text{mol}\cdot\text{L}^{-1}$ HNO_3 (Analytika, Czech Republic) or 0.1 $\text{mol}\cdot\text{L}^{-1}$ NaOH (Mikro Chem, Slovak Republic).

Specific surface area was determined by the ethylene glycol monoethyl ether (EGME) method as well as the values of specific surface area for **JP** is 459 $\text{m}^2\cdot\text{g}^{-1}$ and for **L** 386 $\text{m}^2\cdot\text{g}^{-1}$, respectively. Cation exchange capacity (CEC) was determined by the ammonium acetate method.³² CEC of **JP** is 78.9 $\text{mmol}\cdot 100\text{ g}^{-1}$ and for **L** 40.5 $\text{mmol}\cdot 100\text{ g}^{-1}$. The detailed procedures were presented in the work Brtáňová *et al.*²⁹

Batch adsorption experiments were carried out at 20°C in 250 mL Erlenmeyer flasks by mixing 0.5 g of the adsorbent with 100 mL of Pb^{2+} solution. 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 pH meter Model 340 (WTW, Germany). After 120 min, the suspensions were centrifuged and the solutions were analysed by atomic absorption spectrometry (AAS). The concentrations of the lead before and after adsorption were determined using an atomic adsorption spectrometer AVANTA Σ (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 $\text{mg}\cdot\text{L}^{-1}$) and 261.4 nm (to 500 $\text{mg}\cdot\text{L}^{-1}$). 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 $\pm 5\%$.

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

RESULTS AND DISCUSSION

The metal ions removal process is complex and dependent on the chemistry of the metal ions, specific surface properties of the adsorbents and physicochemical influence such as pH, temperature and metal concentration. The ability of adsorbents to adsorb Pb²⁺ ions from aqueous solution was studied under various optimised conditions of pH, adsorbent dosage, concentration of metals and contact time. The results were expressed as the amount of adsorbed metal ions per mass unit of sorbent at time q_t (mg·g⁻¹) and as the removal efficiency of the adsorbent towards metal ions or the % removal. These variables were calculated by the equations:

$$q_t = \frac{(c_o - c_t)V}{m} \quad (1)$$

and

$$Ads.(\%) = \frac{c_o - c_t}{c_o} 100 \quad (2)$$

where c_o is the initial concentration of metal ions (mg·L⁻¹), c_t is the concentration of metal ions left in aqueous solutions at time t (mg·L⁻¹), V is the volume of the aqueous phase (L) and m is the amount of the bentonite (g).

Effect of pH

The pH of the solution is a major factor in the metal ion removal to competing effect of cation with proton (H⁺). In highly alkaline medium Pb²⁺ ions can

be transformed to hydroxides that are hardly soluble and they precipitate. The adsorption of Pb²⁺ ions on bentonite was examined from solution at initial pH values between 2 and 6. The results presented in Fig. 1 revealed that the adsorption of Pb²⁺ increased when the initial pH of the solution was increased from 2 to 4 and then reached a plateau at pH > 4. 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.³⁴

As the pH increased, exchangeable ions (i.e. Na⁺, K⁺, Ca²⁺ and Mg²⁺, present at the exchangeable sites of bentonite) were exchanged for Pb²⁺ ions in the aqueous solutions. The basic mechanisms that govern the adsorption characteristics of bentonite are adsorption and ion exchange. However, at pH values higher than 5, metal ions were transformed to poorly soluble hydroxides which precipitated such that the aqueous concentrations were below the detection limit.

Effect of adsorbent dosage

The dependence of Pb sorption on adsorbent dosage was studied by varying the amount of adsorbents from 0.1 to 1 g per 100 mL of solution, while keeping other parameters (pH, concentration, and contact time) constant. As shown in Fig. 2, the adsorption percentage of removed lead increases with increasing adsorbents doses from 0.1 g to 0.5 g. It must be also noted that there was non-significant increases in removal percentages when adsorbents dose was increased from 0.5 g to 1 g.

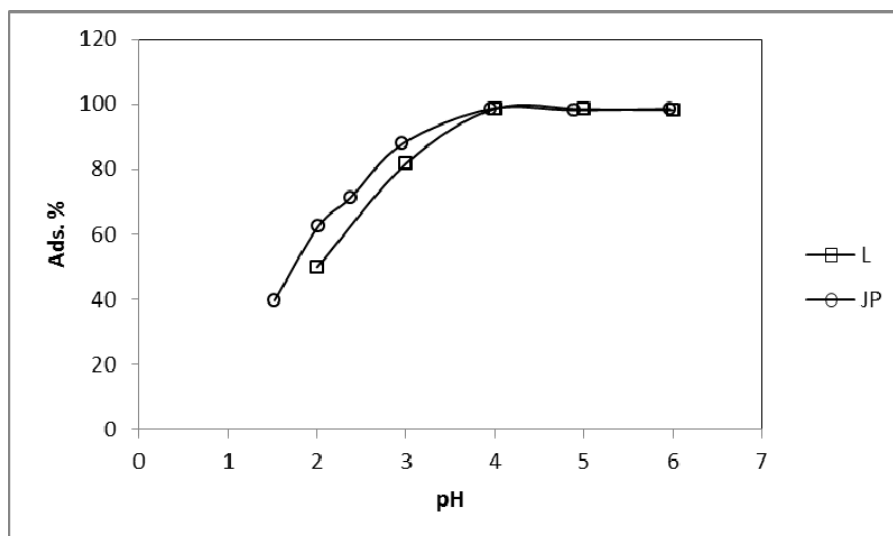


Fig. 1 – Effect of pH on the adsorption of Pb²⁺ ions on *L* and *JP*.

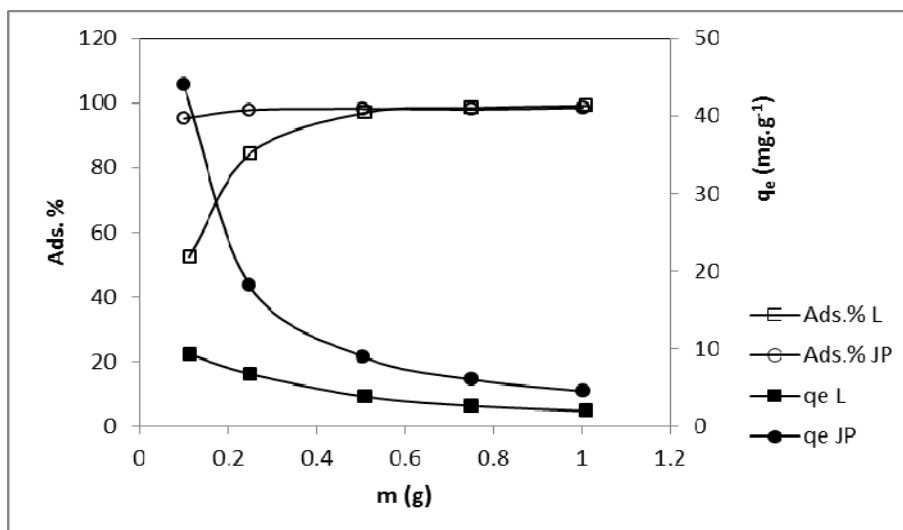


Fig. 2 – Effect of the dosage of bentonite on the adsorption of Pb^{2+} ions on *L* and *JP*.

This suggests that with a certain dose of adsorbent, the maximum adsorption is attained and hence the amount of ions bound to the adsorbent and the amount of free ions remains constant even with further addition of the dose of adsorbent. The increase in the adsorption percentage with an increase in adsorbent dosage is due to the greater availability of the exchangeable sites or surface area at higher concentration of the adsorbent. The adsorption percentage was higher when bentonite from *JP* was used. However, the adsorption capacity of Pb^{2+} ions was observed to decrease with an increase in adsorbent dosage. The adsorbent dosage mass was fixed at 0.5 g per 100 mL of solution for further studies.

Effect of time

The effect of contact time on the adsorption of Pb^{2+} ions on *L* and *JP* was followed for 1 hour. For both sorbents we have observed rapid initial uptake of absorption of Pb^{2+} ions within the first few minutes of the process, similarly to Cu^{2+} ions.²⁹ There was a quick exchange of Pb^{2+} with the cations on the surface and the interlattice edges, followed by a slower reaction of Pb^{2+} diffusion into the pores. Fig. 3 shows an example for time dependence observed for *L*. The measured results show that one hour was sufficient to study the influence of time for sorption properties of the sorbents.

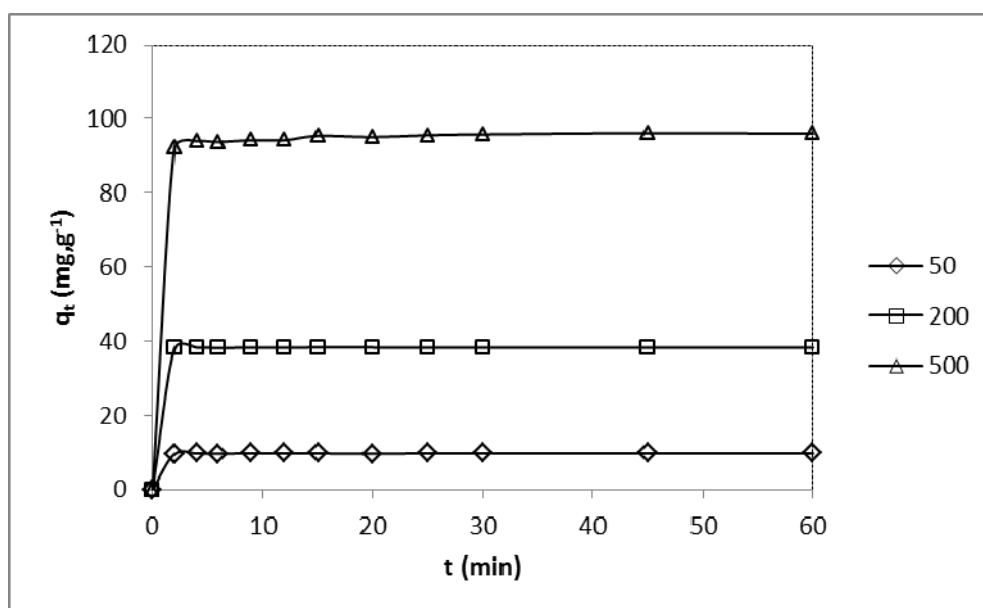


Fig. 3 – Effect of time on the adsorption of Pb^{2+} ions on *L* for various initial concentrations of Pb^{2+} ions. Initial concentration of Pb^{2+} in the legend is given in $mg \cdot L^{-1}$.

Effect of initial Pb²⁺ concentration

The effect of the initial concentration of Pb²⁺ ions was studied in the concentration range 50 - 500 mg·L⁻¹ in the solution at pH 4, with a constant amount of bentonite (0.5 g per 100 mL of solution). From Fig. 4, it can be seen that the adsorption of Pb²⁺ (Ads. %) decreases with an increased initial Pb²⁺ concentration, while the equilibrium adsorption capacity of the bentonite, q_e , showed the opposite trend. It is interesting to note that in the case of JP for Pb²⁺ concentrations greater than 400 mg·L⁻¹ decreases this value.

Adsorption isotherms

Adsorption isotherms provide valuable information on optimizing the use of adsorbing agents. The sorption data with the initial concentration of 50-500 mg·L⁻¹ at pH 4 have been correlated with two most commonly isotherms models – Freundlich and Langmuir. 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. This isotherm was applied in a linear form

$$\log q_e = \log K_F + \frac{1}{n} \log c_e \quad (1)$$

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), 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 favourable, and K_F is the surface adsorption equilibrium constant (mg·g⁻¹).

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

$$\frac{c_e}{q_e} = \frac{1}{b q_m} + \frac{1}{q_m} c_e \quad (2)$$

where q_m is the maximum adsorption capacity corresponding to the monolayer adsorption capacity (mg·g⁻¹) and b is the Langmuir coefficient representing the equilibrium constant related to the adsorbate–adsorbent affinity (L·mg⁻¹).

All solutions contained a fixed mass of bentonite (0.5 g of bentonite per 100 mL of solution). The experimental data were plotted as $\log q_e$ versus $\log c_e$ and c_e/q_e versus c_e respectively and are shown in Figs. 5 and 6. Freundlich adsorption constants (K_f and n) and Langmuir adsorption constants (q_m and b) were calculated from the intercepts and slopes of these linear plots. Utilization of the isotherm equations was compared on the basis of correlation coefficients R^2 . The Langmuir model ($R^2 = 0.997 - 0.999$) yielded in clearly better fits for the adsorption of Pb²⁺ on studied bentonites than the Freundlich model ($R^2 = 0.592 - 0.973$). The calculated results and correlation coefficients (R^2) are listed in Table 1.

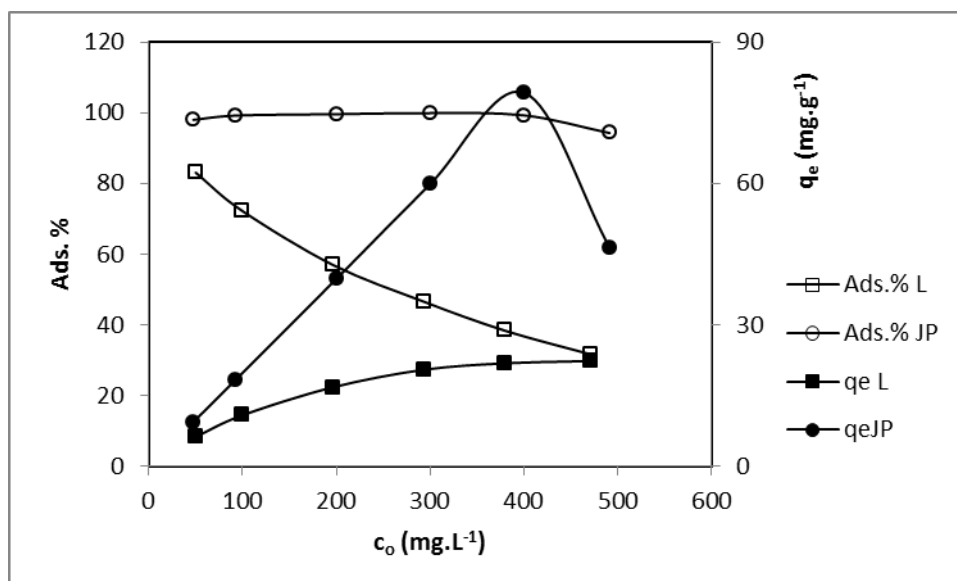


Fig. 4 – Effect of the initial metal concentration on the adsorption of Pb²⁺ ions.

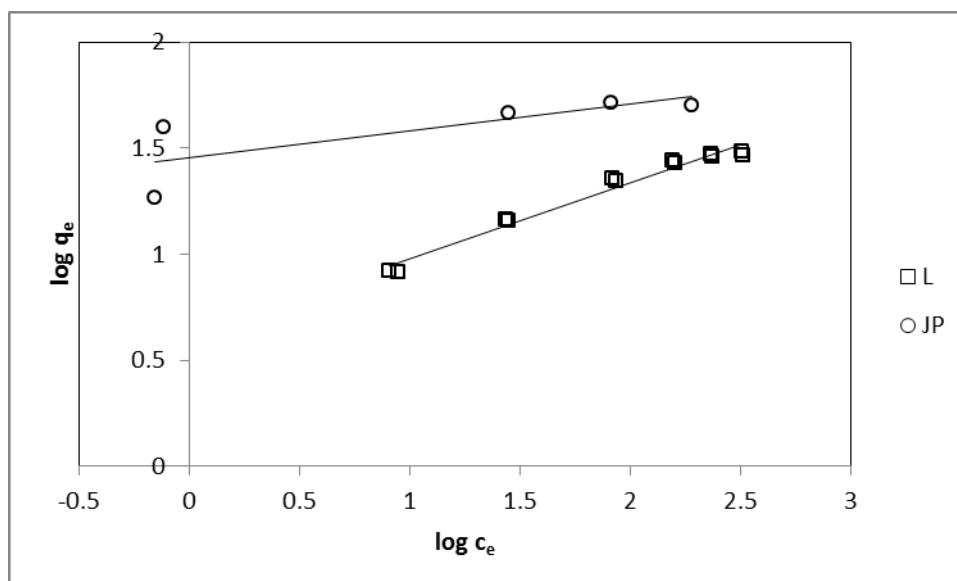


Fig. 5 – Freundlich adsorption isotherm.

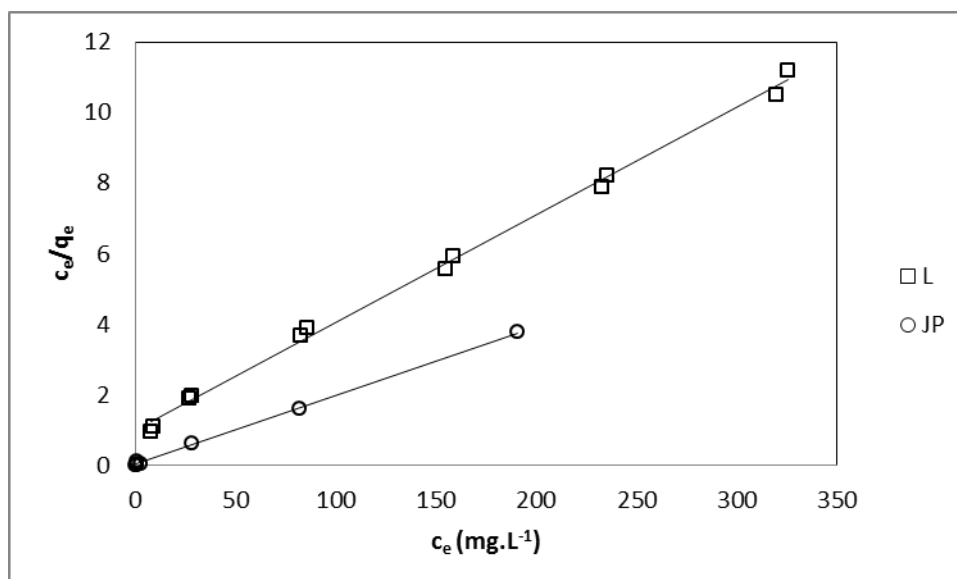


Fig. 6 – Langmuir adsorption isotherm.

Table 1

Parameters of the Freundlich and Langmuir isotherms

Bentonite	Freundlich			Langmuir		
	K_f	n	R^2	q_m	b	R^2
L	4.17	2.79	0.9734	32.68	0.03	0.9972
JP	28.48	7.94	0,5920	51.02	1.02	0.9992

The values of q_m were found to be 32.7 mg of Pb per gram of **L** bentonite and 51.0 mg of Pb per gram of **JP** bentonite, under the optimum adsorption conditions.

Several researchers have studied the adsorption capacity of bentonite samples. The comparison of the

bentonites from Lieskovec and Jelšový Potok with bentonites of similar composition in terms of adsorption capacity for Pb^{2+} ions from aqueous solution at laboratory temperature is given in Table 2.

Table 2

Values of maximum sorption capacities of some bentonites for Pb²⁺ ions

Sorbent	bentonite (Turkey)	granular bentonite (Romania)	natural bentonite	natural bentonite (Turkey)	bentonite (Merck)	<i>L</i>	<i>JP</i>
q _m (mg.g ⁻¹)	16.66	19.45	107	77.82	7.56	32.68	51.02
[Ref]	9	10	12	13	17	This study	This study

CONCLUSIONS

In this study, the adsorption of Pb²⁺ ions on Slovak bentonites was investigated in detail. The initial pH of the aqueous solution is an important parameter in the adsorption process affecting the adsorption of Pb²⁺ ions. The affinity of the adsorption sites for lead is influenced with the pH and is increased with higher pH values of the solution. By increasing the adsorbent dosage, the amount of Pb²⁺ ions adsorbed per unit mass of the adsorbent decreased at equilibrium. Raising the initial metal ion concentration led to an increase in Pb²⁺ uptake by bentonite.

The Langmuir and Freundlich equations were used to fit the equilibrium isotherm, the adsorption isotherms could be well fitted by the Langmuir equation. The greatest adsorption capacity of Lieskovec and Jelšovský Potok bentonites for Pb²⁺ ions was 32.7 and 51.0 mg.g⁻¹, respectively. The results indicate that bentonites used in the experiment could be successfully utilized for the adsorption of Pb²⁺ from aqueous solutions and can be effectively used for the removal of lead from wastewater.

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