ADSORPTION PROCESSES OF LEAD IONS ON THE MIXTURE SURFACE OF BENTONITE AND BOTTOM SEDIMENTS

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ABSTRACT

The adsorption of contaminants plays an important role in the process of their elimination from a polluted environment. The effectiveness of procedures also depends on the properties of the used sorption material. Therefore it is important to study adsorption processes and adsorption kinetics allowing us to describe uptake mechanisms. This work describes the issue of loading environment with lead(II) and the resulting negative impact it has on plants and living organisms. It also focuses on bentonite as a natural adsorbent and on the adsorption process of Pb(II) ions on the mixture of bentonite and bottom sediment from the water reservoir in Kolíňany (SR). The equilibrium and kinetic experimental data were evaluated using Langmuir isotherm kinetic pseudo-first and pseudo-second-order rate equations the intraparticle and surface diffusion models. The thesis obtained from the results suggest that bentonite is suitable for the protection of agricultural land being treated with bottom sediment contaminated by lead. Langmuir isotherm model was successfully used to characterize the lead ions adsorption equilibrium on the mixture of bentonite and bottom sediment. The pseudo second-order model, the intraparticle and surface (film) diffusion models could be simultaneously fitted the experimental kinetic data.

Keywords: adsorption isotherms, adsorption kinetics, bentonite, bottom sediment, lead

1.   Introduction

The plumbum (Pb) as a non-essential element belongs to the group of heavy metals. Their various utilization and processing are also connected with the pollution of environment and endangering of living organisms.

Anthropogenic sources in connection with atmospheric deposition present 80–90% of total Pb distribution to the soil. The Pb is also accumulated in bottom sediments to which Pb is input from water sources. Sediments can be sequentially applied to the soil and result of this process is their contamination. In the respect with permanent problem of environmental endangering by contaminants, e. g. heavy metals, new and more effective processes and technologies for their elimination are still finding and generating. The one of important methods, because of its simplicity and effectivity, is the adsorption. This method is also suitable from the aspect of cost effective natural adsorption materials and their use. The mentioned problem was described by Hefne *et al.* (2008), Sabová *et al.* (2010) Awala and Jamal (2011) and other authors.

This study is focused on adsorption properties of bentonite in the bottom sediment. In addition it is also oriented on the adsorption kinetics of Pb(II) ions from the water medium on the mixture of bentonite and bottom sediment. Experimental data were analysed by using of Langmuir

isotherm and other models describing adsorption mechanism – pseudo first- and second-order, intraparticle and surface diffusion model.

2. Material and methods
2.1. The preparation of samples for determination of adsorption isotherms
For determination of adsorption isotherms, 0,050 g of bottom sediment (water reservoir in Kolíňany, 2011) with bentonite was weighted into glass tubes. After that, 50 ml of $Pb(NO_3)_2$ solution with 6 different Pb concentrations was added. In this experiment, 6 mixture series of bottom sediment with bentonite (from 0 % to 1.00 % of bentonite) was used. We applied 10 treatments of different concentrations of Pb(II) ion solution (from 0.0 mg Pb/L to 160 mg Pb/L).The pH value of aqueous suspension of mixture consisted of bentonite and sediment was adjusted at 6.5 (HNO_3 c = 0.01 mol/L; NaOH c = 0.05 mol/L). Adjusted water suspensions was shaken within 48 hours at the laboratory shaker at t = 23 °C. Samples were sequentially separated within 2.5 min at the centrifuge at 9 000 speed/min. The Pb content in solution was measured at the atomic absorption spectrophotometer with flame atomization (217 nm; volume of measured sample = 10 µl; modifier – $Pd(NO_3)_2$ with c = 0.1 mol/L; 1% of ascorbic acid solution). From obtained values, the amount of adsorbed substance per unit weight of adsorbent in balance q_e (mg/g).

2.2. The preparation of samples for measurement of lead ion adsorption kinetics
The adsorption kinetics of Pb(II) ions was determined on the same mixture of bottom sediment and bentonite by using of two Pb concentration levels. We weighted 0.50 g of 0.50% bottom sediment and bentonite mixture. Into this mixture, we added 250 ml of Pb(II) ion solution with concentration of 30 mg Pb/L and 50 mg Pb/L The prepared colloid solution was sequentially mixed at magnetic mixer at 23 °C. After that, the 10 mL of solution was taken in following time intervals: 2; 5; 10; 15; 20; 25; 30; 40; 50; 60; 90; 120; 150; 180 and 210 minutes. Measured samples of solution were centrifuged within 2.5 min at 9000 speeds/min. From centrifuged samples, the 3 mL of solution was pipetted. At this sample, Pb concentration was determined at the atomic absorption spectrophotometer with flame atomization. The adsorption kinetics of Pb(II) ions was evaluated by using of linearized equations for kinetic models of pseudo-first and pseudo-second order and equations of intraparticle and surface diffusion.

3. Results and discussion
3.1. The evaluation of adsorption capacity
If the concentration of heavy metal is considered as an affecting parameter on the adsorption process, it is possible to observe the increase of adsorption capacity with increasing Pb(II) ion concentration in the range from 0.00 to 160 mg/L and its decrease with increasing bentonite content in the sediment (see Table 1). From mentioned values, it is possible to state that the adsorption capacity of bottom sediment and bentonite is decreasing in relation with increasing Pb concentration and percentage content of bentonite. It means that the bottom sediment adsorbs lower amount of Pb(II) ions after bentonite addition in the mixture.

Table 1: The adsorption capacity of bottom sediment in the mixture with bentonite (t = 23 °C).

–	Pb [mg/L]									
C_0 (mg/L)	0	10	20	30	40	50	70	80	100	160
Sediment – bentonite 0,00%										
C_e (mg/L)	0	0	0	0	3.3	7.5	22.8	33.0	43.0	92.0
q_e (mg/g)	0	10.0	20.0	30.0	36.7	42.5	47.2	47.0	57.0	68.0
Sediment – bentonite 0.10%										
C_e (mg/L)	0	0	0.5	1.9	3.1	7.6	24.5	31.3	45.5	98.1
q_e (mg/g)	0	10.0	19.5	28.1	36.9	42.4	45.5	48.7	54.5	61.9

Sediment – bentonite 0.25%										
Ce (mg/L)	0	0	0	0	3.2	9.9	27.5	30.9	45.8	108.2
qe (mg/g)	0	10.0	20.0	30.0	36.8	40.1	42.5	49.1	54.2	51.8
Sediment – bentonite 0.50%										
Ce (mg/L)	0	0	0.2	0.8	5.5	16.4	22.6	32.4	48.0	106.2
qe (mg/g)	0	10.0	19.8	29.2	34.5	33.6	47.4	47.6	52.0	53.8
Sediment – bentonite 0.75%										
Ce (mg/L)	0.3	0.8	0.8	2.6	5.9	11.8	28.8	35.8	50.9	108.9
qe (mg/g)	-0.3	9.2	19.2	27.4	34.1	38.2	41.2	44.2	49.1	51.1
Sediment – bentonite 1.00%										
Ce (mg/L)	1.2	1.1	1.6	2.0	4.3	12.9	31.7	41.1	53.8	109.0
qe (mg/g)	-1.2	8.9	18.4	28.0	35.7	37.1	38.3	38.9	46.2	51.0

3.2. The evaluation of adsorption equilibrium using Langmuir isotherm model

The values of the Langmuir constants calculated using the least-squares fitting along with correlation coefficients (R^2) are summarized in Table 2. Values in Tables 1 and 2 indicate that adsorption capacity is increasing in relation with increasing Pb(II) concentration in the suspension of mixtures and bottom sediment, and decreasing with increasing amount of bentonite in the mixture material.

The correlation coefficients were high (R^2 = 0.826–0.996) at all cases. Thus, this model is suitable for interpretation of Pb(II) ion adsorption on sediment and bentonite/sediment mixtures. Freundlich isotherm model could not be used for calculation of adsorption constants. It shows evidence of monolayer coverage of homogeneous adsorbent surface (see Table 2). The values of calculated maximum adsorption capacity q_{max} are higher than the experimentally estimated values. The Langmuir constant K_L is an indicator of the stability of combination between adsorbate and adsorbent surface and a constant related to the free energy or net enthalpy of adsorption (Febrianto *et al.*, 2009, Limousin *et al.*, 2007). As shown in Table 2. the Langmuir constant K_L is increasing with increasing of bentonite concentration in the mixture in the range of 0.32–0.41 L/mg.

Table 2: Adsorption constants and correlation adsorption coefficients for Pb(II) ions in the solution on the mixture of sediment and bentonite

Bentonite concentration in the mixture (%)	Langmuir isotherm		
	K_L (L/mg)	q_{max} (mg/g)	R^2
0.00	0.32	65.36	0.973
0.10	0.34	60.98	0.989
0.25	0.88	52.08	0.996
0.50	0.41	54.05	0.992
0.75	-	46.30	0.834
1.00	-	45.46	0.826

Hefne *et al.* (2008) evaluated experimental data by using of Freudlich and Langmuir equations. Authors indicated that Langmuir model is more suitable for evaluation of equilibrium. Andrejkovičová *et al.* (2010) studied the sorption of heavy metals - Pb(II). Cd(II). Cu(II) and Zn(II) - on liparite and andesite bentonite from the middle Slovakia. Authors also found that adsorption is controlled by both isothermal models. Ketcha Mbadcam *et al.* (2011) similarly applied Langmuir and Freudlich isotherm models for evaluation of Pb(II) ion adsorption on

kaolinite and smectite in the decontamination of waste water. Authors found that the adsorption capacity of both minerals was increased with increasing metal concentration, as it was presented in our experiment. In the case of smectite the adsorption equilibrium was described by both models, the correlation coefficients were higher with application of Freundlich isotherm model.

3.3. The evaluation of adsorption kinetics using pseudo first- and pseudo second-order kinetic models

For evaluation of adsorption kinetics for our experimental data was performed by using of pseudo first-, pseudo second-, intraparticle and surface diffusion models. Corresponding rate constants and adsorption capacity values were calculated and summarized with correlation coefficients R^2 in Table 3.

Correlation coefficients and the comparison of experimental and calculated adsorption capacity values indicate that pseudo-second order model of is more suitable for interpretation of adsorption kinetics of Pb(II) ions on the mixture of bottom sediment and bentonite. The theoretical adsorption capacity $q_{eq,cal}$ values show in all cases a very good agreement with the experimentally measured values q_{exp} using second-order model. Pseudo first-order model could not be used for evaluation of kinetic data. It should be taken into consideration that the rapid adsorption process can affect the kinetic modelling.

Similar results were presented by Sabová *et al.* (2010) in the study of water decontamination by using of zeolite adsorbents. In the work of Pb(II) ions adsorption on kaolinite and smectite five kinetic models were used by Ketcha Mbadcam *et al.* (2011) for evaluation of kinetics. Among all these models, the kinetic model of pseudo-second order was proved as most suitable for experimental data. Hefne *et al.* (2008) focused the adsorption possibilities of natural bentonite and presumed that chemisorption is the rate-limiting step in the kinetics of process.

Table 3: Pseudo-first and –second order adsorption kinetic constants for Pb(II) ion adsorption on the bottom sediment/bentonite mixture in aqueous suspension

Pb(II) ion concentration (mg/L)	$q_{e,exp}$ (mg/g)	Velocity equation of pseudo-first order model			Velocity equation of pseudo-second order model		
		k_1 (1/min)	q_e (mg/g)	R^2	k_2 (g/mg.min)	q_e (mg/g)	R^2
30	13,5	0,015	3,955	0,945	0,014	13,986	0,998
50	20,5	0,003	1,801	0,017	0,016	20,243	0,991

3.4 Evaluation of adsorption diffusion models

According to results presented in the Table 4. none of linear dependencies run through beginning of vector basis. It shows that both intraparticle and surface diffusions are separately not the speed determining steps in Pb(II) ion adsorption on the mixture of bottom sediment and bentonite. The adsorption kinetics is probably controlled inter-element and surface diffusion at the same time.

Table 4: Constants calculated from intraparticle diffusion and surface diffusion models for adsorption kinetics for Pb(II) ions from solution on the bentonite/sediment mixture

Pb(II) ion concentration (mg/L)	Model of intraparticle diffusion			Model of surface diffusion		
	k_{ip} (mg/g.min^{0,5})	section	R^2	k_{fd} (1/min)	section	R^2
30	0.279	10.001	0.913	0.015	1.263	0.945
50	0.268	16.635	0.305	0.003	2.433	0.013

4. Conclusion

Experimental data confirm that the increasing Pb concentration results in the higher adsorption capacity and decreased specific adsorbed amounts with increasing bentonite content in bentonite/sediment mixture. It means that the studied natural mixed adsorbent material is characterized by high adsorption capacity for Pb(II) ions.

According to obtained results the increase of percentage content of bentonite in the mixture with bottom sediment tended to decrease of its adsorption capacity at the same Pb contamination level. This fact indicates that the application of modified bottom sediment (by this way) on the agricultural soil results in its decreased contamination by lead.

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