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Removing lead from aqueous solutions using different low-cost abundant adsorbents

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ABSTRACT

The removal of Pb(II) ions from synthetically prepared solutions by different low-cost adsorbents (waste polyurethane foam, Slovak bentonite, and zeolite) was investigated. The adsorption experiments were carried out under a batch process with the concentration of Pb(II) ions, amount of adsorbent, pH, and time as the variables. Adsorption was strongly dependent on the pH of the medium, with the uptake of Pb(II) increasing as the pH increased from pH 1.5 to 5.0, after which the experiments could not be continued due to the decreasing solubility of Pb(II). The adsorption was very fast at low coverage, and equilibrium was approached within 60 min. The results best fitted the second-order kinetic model, with the rate constant in the range of 3.0×10^{-2}–2.9 g/mg min. The Langmuir maximum adsorption capacity of the waste polyurethane foam, zeolite, and bentonite was found to be 14.1, 43.9, and 48.1 mg/g, respectively.

Keywords: Bentonite; Zeolite; Waste polyurethane foam; Adsorption; Lead

1. Introduction

The occurrence of metals in wastewater is associated with the development of industry and agriculture. A serious problem is presented by toxic metals entering into water, mainly through wastewater from mining activities, metallurgy, surface treatment of metals, agriculture, and different other industries. Metal toxicity and the forms in which it occurs depend on the temperature, pH, and overall composition of the water. Most toxic effects are due to simple ionic forms, while inorganic and organic complexes are generally less toxic. Some metals are characterized by their ability to pass from the liquid phase to a solid, which accumulates in the body. Metals with a high coefficient of accumulation are Hg, Pb, Zn, and Cu.

Lead and lead compounds are considered among the major toxic contaminants in the environment. They can enter into the environment through soils and water streams from various industrial activities such as metal plating, oil refining, and battery manufacturing. Lead can enter the human body via inhalation, ingestion, or skin adsorption. It damages the kidneys, liver and reproductive system, brain functions, and basic cellular processes. Toxic symptoms include anemia, insomnia, headache, dizziness, irritability, muscle weakness, and hallucination [1,2].

A number of technologies for the removal of metal ions from aqueous solutions have been developed over the years [3,4]. Traditional methods include

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chemical precipitation, ion exchange, reverse osmosis, electrochemical methods, solvent extraction, and adsorption on activated carbon. However, most of these methods have some disadvantages such as high cost, a complicated treatment process, or high energy use. With adsorption methods, the main disadvantage is the high price of the adsorbents, which increases the price of wastewater treatment. The development of low-cost adsorbents and their ease of application, regeneration, and reuse have made adsorption from the liquid phase an attractive process for treating contaminated water. Various adsorbents have been investigated for removing lead ions from aqueous solutions; for example, bentonite [1,5–9], and zeolite [9–12] have found use as adsorbents.

The main constituent of bentonite is montmorillonite, a clay 2:1 mineral from the smectite group with one octahedral sheet and two tetrahedral silica sheets that form a single layer [13]. The layers are held together by van der Waals forces. Isomorphous substitutions in the layers are responsible for a negative charge. Because of these weak forces and some charge deficiencies in the structure, water can easily penetrate between the layers so dissolved cations can balance the deficiencies [13]. Bentonite is considered as the best backfill material for the disposal of radioactive nuclear waste and has been studied intensively [14–17].

Zeolites are naturally occurring aluminosilicates with a porous three-dimensional framework. The basic structural units are $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedral, which are linked to each other by sharing all of their oxygen atoms to form interconnected cages and channels [18] where exchangeable cations are present. Their presence counterbalances the negative charge on the zeolite surface generated from isomorphous substitution [19,20].

Polyurethane foam materials represent an important class of thermoset and thermoplastic polymers, as their mechanical, thermal, and chemical properties can be tailored by the reaction of various polyols and polyisocyanates [21]. Rigid polyurethane foam is the most widely used insulting material throughout the world for refrigerators and freezers. Polyurethanes in general are widely used, inevitably leading to the production of a large amount of polyurethane foam waste which is recycled in two primary ways: mechanical recycling, in which the material is reused in its polymer form, and chemical recycling that returns the material back to its various chemical constituents [22].

The aim of our work was to study the adsorption of Pb(II) ions on low-cost abundant adsorbents. Specifically, we intended (1) to investigate the effectiveness of adsorbents in removing Pb(II) from aqueous solutions and (2) to study the effects of pH, Pb(II) concentration and amount of adsorbent on the adsorption capacity of the adsorbents.

2. Materials and methods

2.1. Reagents

The aqueous solutions of lead ($Pb(NO_3)_2$, MikroChem, Slovakia) used in experiments were prepared with water deionized by reverse osmosis (Demiwa, Watek, Czech Republic). All chemicals were of analytical reagent grade and were used without further purification. The pH of the solutions was adjusted by addition of 0.1 mol/l HNO_3 (Analytika, Czech Republic) or 0.1 mol/l NaOH (MikroChem, Slovakia) as needed.

2.2. Sample preparation

Three different materials from Slovakia were examined for their removal of Pb(II) ions from aqueous solutions. Powdered bentonite was obtained from the Jelšový potok deposit (central Slovakia). This deposit is currently mined by Envigeo Inc., Slovakia. Zeolite was obtained from the Nižný Hrabovec deposit, which is currently mined by Zeocem Inc., Slovakia. Waste polyurethane foam originated from the recycling line of refrigerators and was supplied by Elektrorecycling Ltd. (Slovenská Ľupča, Slovakia). Samples of adsorbents were used as obtained without further purification. Samples were dry-sieved under open laboratory conditions using a standard mesh (<200 μm) sieve and dried in Petri dishes in a drying oven at a temperature of 105˚C for approximately 2–3 h; then, they were placed into small polypropylene containers and laid inside a desiccator, where they were stored till further use.

2.3. Apparatus and analytical procedure

The ability of each adsorbent to adsorb Pb(II) ions from aqueous solution was studied under different optimized conditions of pH, adsorbent dosage, metal concentration, and contact time.

Batch adsorption experiments were carried out at 20˚C in 250-ml Erlenmeyer flasks by mixing 0.5 g of adsorbent with 100 ml of a lead solution. The initial pH of the solutions was adjusted with HNO_3 or NaOH to a desired value. The time to reach equilibrium was 120 min. The pH values of all solutions were measured using a Model 340 pH meter with a SenTix41 electrode (WTW, Germany).

To study the effect of the amount of each adsorbent used, the amounts of bentonite (from 0.1 to 1.0 g), zeolite (0.1–1.0 g), and polyurethane foam (0.1–0.7 g) added were each varied. The other parameters were as follows: pH 4; initial concentration of Pb(II) ions 50 mg/l; and time to reach equilibrium 120 min.

To study the effect of the initial concentration of lead ions, solutions with concentrations ranging from 50 to 500 mg/l at pH 4 were used with a constant amount of adsorbent (0.5 g per 100 ml of solution).

The effect of contact time was tested by mixing 5 g of adsorbent with 1,000 ml of Pb(II) ion solution at different concentrations (50, 200, and 500 mg/l). The pH values of the solutions were not adjusted. The suspension was stirred (200 rpm), and 2-ml aliquots were collected at regular time intervals, centrifuged, and then analyzed for metal ions by atomic absorption spectrometry (AAS).

After mixing for the desired contact time, the suspensions were centrifuged and the solutions were analyzed for metal ions by AAS. Each adsorption experiment was carried out in duplicate using two independent samples. The limit of experimental error between duplicates was less than ±5%.

The concentrations of metal ions before and after adsorption were determined by an AVANTA Σ atomic adsorption spectrometer with acetylene–air flame atomization (GBC Scientific, Australia). The measured data were processed by the GBC Avanta software. The working wavelength for Pb(II) ions was 283.3 nm (to 50 mg/l) and 261.4 nm (to 500 mg/l). The instrument response was periodically checked using standard metal ion solutions.

The amount of adsorbed Pb(II) ions per mass unit of adsorbent at time q_t (mg/g) was calculated by the following equation:

$$q_t = \frac{(C_o - C_t)V}{m} \tag{1}$$

where C_o is the initial concentration of the Pb(II) ions (mg/l), C_t is the concentration of Pb(II) ions left in aqueous solutions at time t (mg/l), V is the volume of the aqueous phase (l), and m is the amount of the adsorbent (g).

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

$$Ads.(\%) = \frac{C_o - C_t}{C_o} 100 \tag{2}$$

3. Results and discussion

3.1. Characterization of adsorbents

Two different minerals and waste polyurethane foam were used in order to examine the removal of Pb(II) from aqueous solutions.

Natural bentonite from the Jelšový potok deposit is used in construction with the addition of Na_2CO_3. It has been shown by previous X-ray analysis on this clay [23] that the dominant component is montmorillonite (82%). Natural zeolite from the Nižný Hrabovec deposit is marketed as Zeocem. It was characterized by the nitrogen adsorption method, scanning electron microscopy, transmission electron microscopy, and the X-ray diffraction [24]. The % concentration of clinoptilolite in zeolite was 84%.

The chemical compositions of the bentonite and zeolite used in the experiments are shown in Table 1.

The composition of the waste polyurethane foam was analyzed by infrared spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, and AAS.

By comparing the experimental FTIR spectra with the spectra of the PU adsorbent in the Hummel/Scholl catalog [25], it was identified as adsorbent polyether urethane based on its polypropylene glycol and diphenylmethane diisocyanate content.

NMR analysis confirmed that the polyurethane foam was a non-homogeneous mixture of polyester-based polyurethane based on alkylene dicarboxylic acids, propylene glycol, butylene glycol, and polyether polyurethane prepared from a polyether polyol based on ethylene oxide and propylene oxide. The urethane component in both types of polyurethane consists of diphenylmethane diisocyanate and toluene diisocyanate [26].

Determinations of heavy metals in ash from polyurethane foam samples and in the original samples (Table 2) were performed using an AA-6501 atomic

Table 1
Chemical compositions of used bentonite and zeolite

	SiO_2 (%)	Al_2O_3 (%)	CaO (%)	Fe_2O_3 (%)	MgO (%)	MnO (%)	Na_2O (%)	K_2O (%)	TiO_2 (%)	P_2O^5 (%)	SO^3 (%)
Bentonite	68.33	20.5	2.03	2.52	4.37	0.07	0.64	1.23	0.18	0.06	0.07
Zeolite	65.0	11.5	2.7	0.7	0.6	–	0.2	2.2	0.1	–	–

Table 2
AAS analysis of the polyurethane foam

Metal	Polyurethane foam ash (mg/kg)	Polyurethane foam sample (mg/kg)
Fe	352,000 ± 35,000	78,000 ± 7,800
Cu	34,900 ± 3,500	7,800 ± 780
Zn	43,200 ± 4,300	9,660 ± 960
Mn	1,830 ± 180	410 ± 41
Pb	1,560 ± 150	350 ± 35

Table 3
Sieve analysis of the polyurethane foam

Percent retained on the sieve								
2,000 μm	1,000 μm	500 μm	250 μm	125 μm	80 μm	63 μm	32 μm	Percent passing through the sieve 32 μm
1.01	5.64	15.02	17.63	38.57	15.09	5.36	1.74	0.023

Notes:Dry matter content at 105˚C: 98.1 ± 0.50 wt%.
Ash at 600˚C: 22.4 ± 0.30 wt%.

absorption spectrometer with flame and electrothermal atomization (Shimadzu, Japan).

3.2. Effect of the quantity of adsorbent

The effect of adsorbent dose on the removal efficiency of Pb(II) ions was studied at different doses (0.1–1 g per 100 ml of solution) (Fig. 1). From Fig. 1, it can be seen that the percent adsorbed increased with increasing amounts of adsorbent. The efficiency of removal of Pb(II) ions from the solution increased up to the optimal doses (98% bentonite, 99% zeolite, and 95% polyurethane foam), after which further increases were negligible. The increased percentage of adsorption with rising adsorbent dosage is due to the increase in the number of active sites on the adsorbent, thus making penetration of the metal ions to the sorption sites easier [27]. Therefore, 0.5 g per 100 ml of solution was selected as the optimum adsorbent dosage for further experiments.

From Fig. 2, it can be seen that the adsorption capacity of the adsorbent gradually decreased with increasing amounts of solid adsorbent particles. The solid adsorbent surface consists of sites with a specific binding energy. At a low dose of adsorbent, a large amount of adsorbate is readily available to be captured by the few available sites. At higher concentrations of solid particles of the adsorbent, the number of binding sites available for the same volume of liquid increases, and thus, the total amount of metal that is removed increases. However, the amount of metal

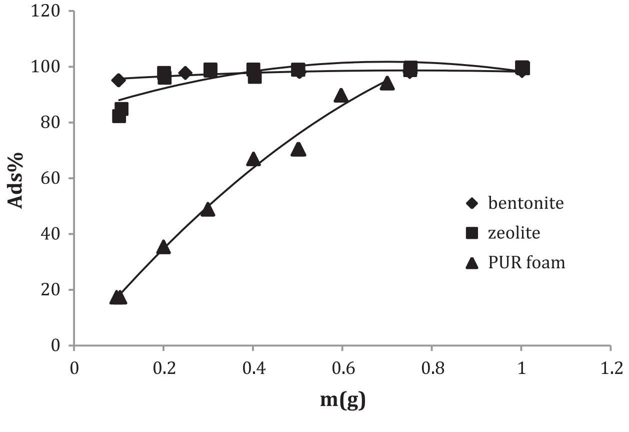

Fig. 1. Effect of adsorbent dose on adsorption of Pb(II) ions (experimental conditions: 100 ml solution, C_o Pb(II) ions 50 mg/l, pH 4, temperature 20˚C).

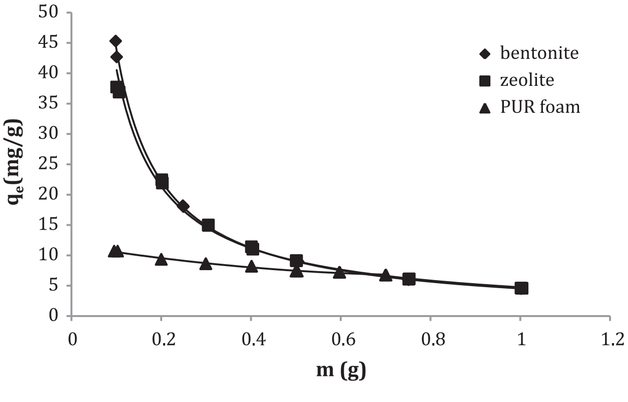

Fig. 2. Dependence of equilibrium adsorption capacity on the amount of different adsorbents.

adsorbed per unit mass decreases. At a high dose of adsorbent, the available metal concentration is insufficient to completely cover the exchangeable sites on the adsorbent, usually resulting in low metal uptake [28]. The addition of adsorbent also affected the pH of the solution, which increased with increasing amounts of adsorbent (bentonite 8.45–10.40, zeolite 5.07–6.43, and polyurethane foam 5.70–6.05). This may be attributed to the increase of the number of negatively charged sites, which can therefore adsorb more H^+ ions, resulting in an increase in the pH of the final solution [28].

3.3. Effect of pH

The effect of pH is an important controlling parameter in adsorption processes. The adsorption of Pb(II) ions on the adsorbents was studied at different pH values ranging from 1.5 to 5.0 for a constant amount of adsorbent (0.5 g per 100 ml of solution). The initial concentration of the metal ion was 50 mg/l. The quantity of Pb(II) ions adsorbed from solution increased as the pH of the initial solution increased, as shown in Fig. 3.

At lower solution pH, binding sites on the adsorbent are positively charged on account of their protonation. This will provide electrostatic repulsion between Pb(II) ions and positively charged binding sites. The result is a low adsorption effectiveness of the adsorbents. At higher pH values, the surface of the absorbent is negatively charged as a result of deprotonation, and electrostatic repulsion decreases with increasing pH. At pH values higher than 4, metal precipitate appeared and the adsorbent deteriorated with the accumulation of Pb(II) ions [29–31]. Therefore, pH 4 was selected as the optimum pH for further studies.

The distribution of the various forms of lead complexes that prevail at a given pH also played an important role in the adsorption of Pb(II) ions from the solution. At pH values less than 7, Pb(II) ions predominate in the solution and the removal is carried out by adsorption and ion exchange. The predominant species at higher pH values are hydroxocomplexes of lead, and thus, their removal from solution can be achieved via precipitation of $Pb(OH)_2$ and adsorption of $Pb(OH)^+$ at the same time. At pH values in the 10–12 range, $Pb(OH)_2$ and $Pb(OH)_3^-$ are the predominant forms of lead; hence, the decrease in adsorption Pb(II) ions on the adsorbent can be partly attributed to the competition between OH^- and $Pb(OH)_3^-$. It is difficult for the negatively charged ions to be adsorbed on the negatively charged surface of the adsorbent at higher pH values due to electrostatic repulsion [7].

3.4. Effect of initial concentration

The initial concentration of the metal in the liquid phase significantly affected the process of adsorption. The effect depends on various factors such as the type of metal removal and the liquid, the availability of functional groups on the surface of the adsorbent, and the ability of these groups to bind metal ions.

With increasing concentrations of Pb(II) ions in solution (50–500 mg/l), there were increases in the amount of metal adsorbed per unit weight of adsorbent (Fig. 4), but on the other hand, there was a reduction in the overall efficiency of Pb(II) ion removal (Fig. 5).

At low initial concentrations of Pb(II) ions, the ratio of metal ions to the amount of adsorbent is low, and thus, adsorption does not depend on the initial

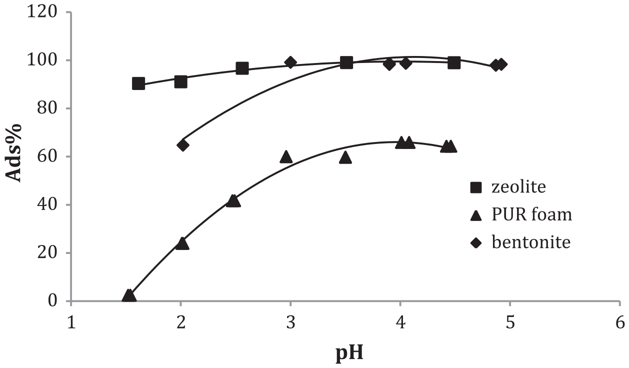

Fig. 3. Effect of pH on adsorption of Pb(II) ions (experimental conditions: 0.5 g adsorbent, 100 ml solution, C_o Pb (II) ions 50 mg/l, temperature 20°C).

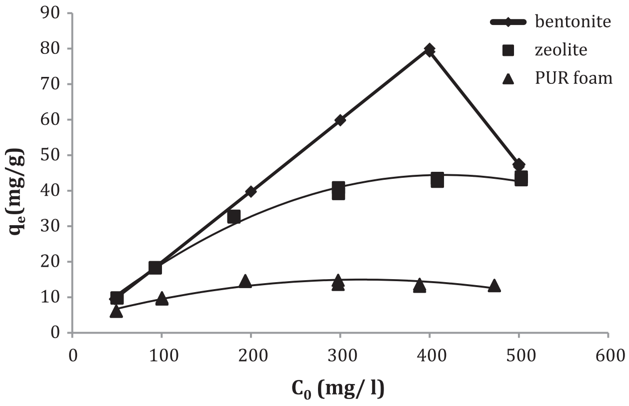

Fig. 4. The dependence of the equilibrium adsorption capacity on the initial concentration of Pb(II) ions (experimental conditions: 100 ml solution, the amount of the adsorbent = 0.5 g, pH 4, temperature 20°C).

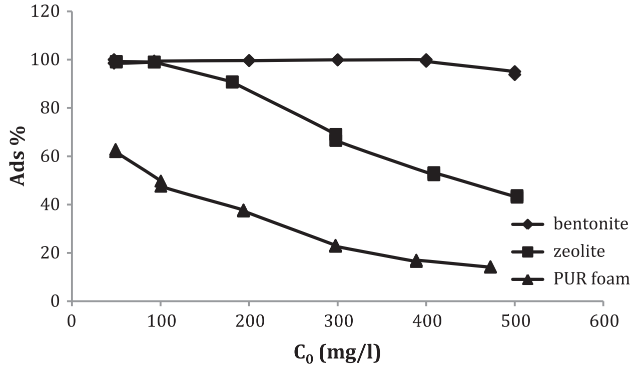

Fig. 5. The effect of initial metal concentration on the adsorption of Pb(II) ions (experimental conditions: 100 ml solution, the amount of the adsorbent = 0.5 g, pH 5, temperature 20°C).

concentration. Subsequent increases in the initial metal concentration increased the quantity of Pb(II) ions adsorbed per unit amount of adsorbent until saturation was reached.

In this case, further increases in the concentration of Pb(II) ions are not accompanied by increases in the amount adsorbed per unit weight of metal. In the case of bentonite at a concentration of 500 mg/l, we even observed a reduction in the amount adsorbed per unit weight of metal.

At low metal concentrations, the surface coverage of the absorbent is low and the formation of surface complexes is the main mechanism. An increase in metal concentration favors the concentration of compounds and aggregates on the adsorbent surface. A further increase in metal concentration results in saturation of adsorption sites, and surface precipitation becomes the main uptake mechanism. Saturation of the active sites is generally faster in cases where an adsorbent exhibits low selectivity for a metal. However, this is not always the case, since metal complexes formed or entrapped in the surface of the adsorbent may accelerate surface saturation even at low concentrations of metals that present high affinity for the adsorbent.

For practical applications, it is important to establish the maximum concentration of Pb(II) ions at which overall saturation of the adsorbent occurs [29].

3.5. Adsorption isotherms

Adsorption isotherms describe the adsorption of a material on a surface at a constant temperature at equilibrium. Adsorption isotherms are obtained from measured data by means of regression analysis. Numerous isotherm equations have been reported, and two major isotherms, the Freundlich and Langmuir isotherms, were applied to establish the relationship between the quantity of Pb(II) ions adsorbed by the adsorbents and their equilibrium concentration in aqueous solution.

The Freundlich isotherm is valid for heterogeneous surfaces and predicts an increase in the concentration of the ionic species adsorbed onto the surface of a solid when the concentration of said species in the liquid phase is increased. The Freundlich isotherm is given as

$$q_e = K_F C_e^{\frac{1}{n}} \tag{3}$$

The linear form of the equation can be written as

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{4}$$

where C_e and q_e are the equilibrium concentrations of Pb(II) ions in the liquid and the solid phases, respectively (mg/l), K_F is a constant related to the adsorption capacity (mg/g), and $1/n$ is an empirical parameter related to the adsorption intensity, which varies with the heterogeneity of the adsorbent. For values in the range $0.1 < 1/n < 1$, adsorption is favorable.

The Langmuir adsorption isotherm assumes that adsorption occurs at specific homogeneous sites on the adsorbent and can be used successfully in many monolayer adsorption processes. It can be expressed as follows:

$$q_e = \frac{q_m b C_e}{1 + b C_e} \tag{5}$$

where q_e is the equilibrium Pb(II) ion concentration on the adsorbent (mg/g), q_m is the monolayer adsorption capacity of the adsorbent (mg/g), C_e is the equilibrium metal ion concentration in the solution (mg/l), and b is the Langmuir adsorption constant, related to free energy of adsorption (l/mg).

The linear form of the equation is given by:

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

Adsorption isotherms of Pb(II) ions on the three used adsorbents are shown in Figs. 6 and 7. Fig. 6 shows the Freundlich isotherms obtained by plotting log qe vs. log C_e values. The values of K_f and $1/n$ were found to be 30.65 and 0.151 for bentonite, 15.13 and 0.207 for zeolite, and 3.84 and 0.220 for polyurethane

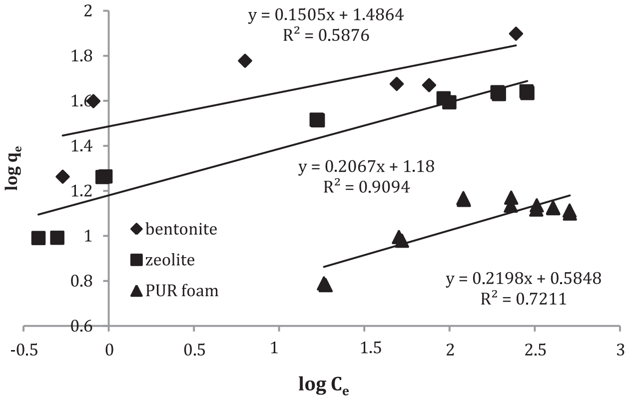

Fig. 6. Freundlich adsorption isotherms.

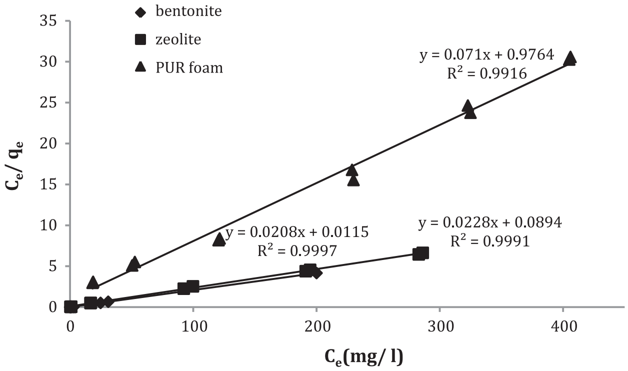

Fig. 7. Langmuir adsorption isotherms.

foam. The $1/n$ values were between 0 and 1, indicating that the adsorption of Pb(II) onto bentonite, zeolite, and polyurethane foam was favorable under the studied conditions. The R^2 value was found to be 0.588–0.909 for Pb(II) ions, indicating that the Freundlich model was unable to adequately describe the relationship between the q_e and C_e values.

Fig. 7 shows the Langmuir isotherm obtained by plotting C_e/q_e vs. C_e values. The value of the maximum adsorption capacity (q_m) was found to be 48.1 mg/g for bentonite, 43.9 mg/g for zeolite, and only 14.1 mg/g for polyurethane foam (Table 4). The Langmuir isotherm model ($R^2 > 0.992$) fitted the equilibrium data better than the Freundlich isotherm model obtained for the adsorption of Pb(II) ions on the used adsorbents. Similar results have been reported for Pb(II) adsorption on different adsorbents by several authors [28].

The Langmuir constant b (l/mg) is used to calculate K_R, a dimensionless separation factor given by the equation [32,33]:

$$K_R = \frac{1}{1 + b\,C_o} \tag{7}$$

where C_o is the initial concentration (mg/l). K_R values reveal whether the adsorption is unfavorable ($K_R > 1$), linear ($K_R = 1$), favorable ($0 < K_R < 1$), or irreversible ($K_R = 0$)

The values of K_R at concentrations of 50–500 mg/l for all three adsorbents are given in Table 5. It is apparent that the adsorption of lead on the used adsorbents is favorable under the conditions used in this study [33,34].

3.6. Effect of contact time

The dependence of the adsorption of Pb(II) ions on time is presented in Fig. 8. It is interesting to note that the percentage of removed Pb(II) ions on the used adsorbents (especially at higher concentrations) achieved the highest values q_t at the beginning of the process. The time to reach adsorption equilibrium increased with increasing initial concentration (50–500 mg/l). The analysis with polyurethane foam was performed only at the lowest concentration (50 mg/l) due to its low density—a large amount of adsorbent was floating on the surface of the solution.

The whole dynamic adsorption process consists of two distinct steps: an initial fast adsorption followed by a much slower adsorption. In the first minutes, adsorption sites are readily available and the Pb(II) ions interact easily with the sites. This initial stage of

Table 4
Parameters of Langmuir and Freundlich isotherms

	Freudlich parameters			Langmuir parameters		
Adsorbent	k (mg/g)	$1/n$	R^2	q_m (mg/g)	b (l/mg)	R^2
Bentonite	30.65	0.151	0.5881	48.08	1.81	0.9997
Zeolite	15.13	0.207	0.9094	43.86	0.26	0.9991
Polyurethane foam	3.84	0.220	0.7211	14.08	0.07	0.9916

Table 5
K_R values calculated from the Langmuir constants

C_o (mg/l)	50	100	200	500
Bentonite	0.011	5.5×10^{-3}	2.8×10^{-3}	1.1×10^{-3}
Zeolite	0.070	0.037	0.019	7.6×10^{-3}
Polyurethane foam	0.220	0.125	0.067	0.028

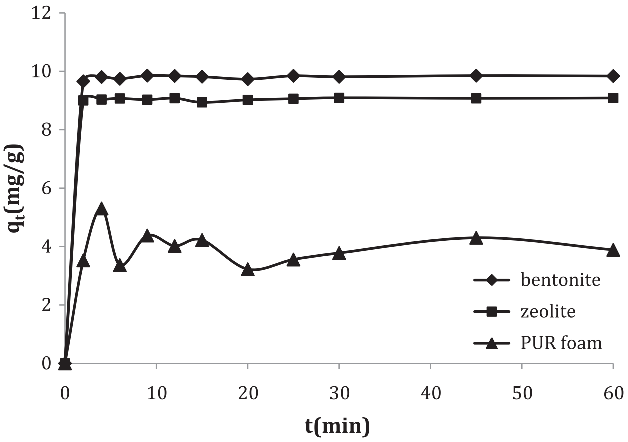

Fig. 8. Effect of time on the adsorption of Pb(II) ions by the used adsorbents (experimental conditions: 1,000 ml solution, 0.5 g adsorbent C_o of Pb(II) ions 50 mg/l, pH 4, and temperature 20˚C).

fast adsorption corresponds to ion exchange in micropores on the surface of the adsorbents [35]. Furthermore, the driving force for adsorption is initially very high and this also results in a higher adsorption rate. However, after the initial period, adsorption may slow due to slower diffusion of ions into the layers (bentonite) or interior channels (zeolite) of the adsorbent, the ions subsequently occupying exchangeable positions within the crystal structure [36,37].

3.7. Kinetics studies

The adsorption equilibrium data were analyzed using two models, pseudo-first-order and pseudo-second-order kinetic models. The linearized form of the pseudo-first-order rate equation by Lagergren [38] is given as

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (8)$$

where k_1 is the pseudo-first-order adsorption rate constant (l/min), and q_t and q_e are the amounts of metal ions adsorbed at time t (min) and at equilibrium, respectively (mg/g). The value of k_1 can be obtained from the slope of the linear plot of ln $(q_e–q_t)$ vs. t.

The plots of ln $(q_e–q_t)$ vs. t for the pseudo-first-order model are not shown in the figure due to the low R^2 values (0.095–0.827) and negative values for the k_1 constant (Table 6). These results show that the adsorption of Pb(II) ions onto each of the used adsorbents does not follow the pseudo-first-order kinetic model.

The experimental data were also tested using the pseudo-second-order kinetic model, which is given in the following linear form [39]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (9)$$

where k_2 is the pseudo-second-order adsorption rate constant (g/mg min), and q_t and q_e are the amounts of

Table 6
Comparison of adsorption rate constants and the experimental and calculated q_e values for pseudo-first-order and pseudo-second-order reaction kinetics of adsorption of Pb(II) ions on the used adsorbents

			Pseudo-first-order			Pseudo-second-order		
Adsorbent	Initial metal concentration (mg/l)	q_e experimental (mg/g)	k_1 (l/min)	q_e calculated (mg/g)	R^2	k_2 (g/mg min)	q_e calculated (mg/g)	R^2
Bentonite	50	9.9	−0.014	0.115	0.225	2.58	9.84	1
	200	38.4	−0.013	0.123	0.095	0.68	38.31	1
	500	96.35	−0.055	3.118	0.827	0.08	96.15	1
Zeolite	50	9.1	−0.309	0.072	0.349	2.02	9.90	1
	200	33.92	−0.035	6.499	0.945	0.68	38.32	1
	500	40.25	−0.054	8.188	0.424	0.03	39.37	0.997
PUR foam	50	4.2	−0.033	0.360	0.154	2.89	3.84	0.995

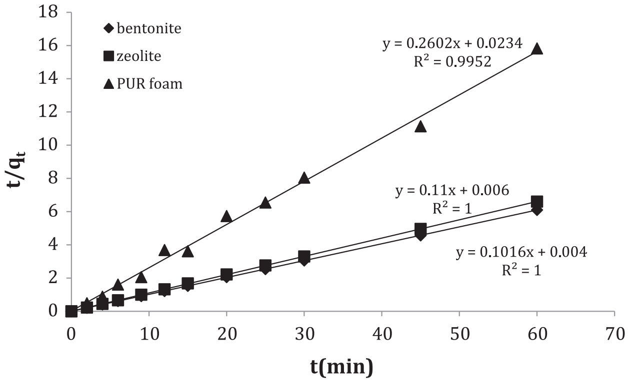

Fig. 9. Pseudo-second- order adsorption kinetics of Pb^{2+} ions on the used adsorbents at an initial concentration of Pb(II) ions of 50 mg/l.

solute adsorbed per unit of adsorbent (mg/g) at time t and at equilibrium, respectively.

The plot of t/q_t vs. t gives a straight line, which allows computation of q_e and k_2. In this study, the initial lead concentration was determined as 50, 100 and 200 mg/l in different trials. The effects of contact time on the removal efficiency of Pb(II) ions using 5 g/l adsorbent at pH 4 are shown in Figs. 8 and 9. It can be seen that the amounts of metal ions adsorbed on the used adsorbents increased with increasing contact time. In each case, the rate of adsorption of Pb(II) ions on the used adsorbents reaches equilibrium in the initial 60 min. The rate constant k_2, the R^2, and the q_e values are given in Table 6. The high R^2 values show that the adsorption of Pb(II) ions onto the used adsorbents closely follows the pseudo-second-order kinetic model and is based on the assumption that the rate limiting step may be chemisorption [27,40]

4. Conclusions

The adsorption of Pb(II) ions increased with increasing pH of the solution. By increasing the adsorbent dosage, the quantity of Pb(II) ions adsorbed per unit mass of the adsorbent decreased at equilibrium. Raising the initial metal ion concentration led to an increase in Pb(II) uptake by the used adsorbents. The adsorption equilibrium was better described by the Langmuir isotherm model than the Freundlich model. The monolayer adsorption capacities of bentonite, zeolite, and polyurethane foam for Pb(II) ions were found to be 48.1, 43.9, and 14.1 mg/g, respectively. As can be seen from these values, the removal efficiency of the adsorbents increased in the order bentonite > zeolite > polyurethane foam. Kinetic examination of the equilibrium data showed that the adsorption of Pb(II) ions onto the used adsorbents closely followed the pseudo-second-order kinetic model.

The results suggest that natural bentonite and zeolite are suitable as adsorbent materials for the recovery and adsorption of Pb(II) ions from aqueous solutions. Despite the higher efficiency of removal of Pb(II) ions from the solution, waste polyurethane foam cannot be used as an adsorbent because of its low density.

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List of symbols

Ads.%	—	the adsorption percentage
b	—	the Langmuir adsorption constant
C_e	—	the equilibrium metal ion concentration in the solution
C_o	—	the initial concentration
C_t	—	the concentration at time t
k_1	—	the pseudo-first-order rate constant
k_2	—	the pseudo-second-order rate constant
K_F	—	a constant related to the adsorption capacity
K_R	—	a dimensionless separation factor
m	—	the amount of the adsorbent
q_e	—	the amount of metal ions adsorbed at equilibrium
q_m	—	the monolayer adsorption capacity of the adsorbent
q_t	—	the amount of metal ions adsorbed at time t
R^2	—	correlation coefficient
t	—	time
V	—	the volume of the aqueous phase
$1/n$	—	an empirical parameter related to the adsorption intensity

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