Original Research

A Comparison of Pb²⁺ Sorption from Aqueous Solutions on Walnut Shells and Plum Stones

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Abstract

This article presents the results of research on the comparison of Pb²⁺ sorption from aqueous solutions on walnut shells with that on plum stones. For walnut shells the depletion of Pb²⁺ in the solution was 62.9-83.7% and for the plum stones, 47.2-81.3%. The effect of various factors, such as the concentration of natural sorbent, pH, and temperature was studied. The process of Pb²⁺ ion sorption on walnut shells and on plum stones was described by the Langmuir and Freundlich models. The maximum sorption capacity of walnut shells was for 23.1 mg/g, whereas for plum stones it was 21.2 mg/g.

Keywords: sorption, lead ions, walnut shells, plum stones

Introduction

Due to the unique toxicity of heavy metals, their presence in natural waters is particularly dangerous for living organisms. This group includes such elements as lead, cadmium, mercury, etc. One of the most harmful heavy metals is lead. Lead emission into the atmosphere comes from smelting and purification of lead and from manufacturing products containing this element. Exposure to lead occurs during the production of batteries, cables, bearings, and wires, and in the chemical industry in the process of manufacturing printing types, dyes, and insecticides. Another source of lead pollution is also Tetraethyllead, added to petrol as an anti-knock additive [1].

Because of the deficiency of drinking water in the world, keeping its good quality has become a particular issue in recent years. The main sources of natural water pollution are industrial and urban waste water, rain water, and leachate from landfills. The concentration of lead in atmospheric water ranges from 1 to 50 µg/L, but in densely inhabited and industrial areas it can reach 1,000 µg/L [2].

Lead can get into drinking water when it is in contact with lead pipes or when stored in containers coated with paints containing this metal. In areas where water is hard and the pH value does not fall below 7.0, the pipes of lead are stable. Calcium, magnesium, and lead carbonates formed in these conditions behave as a protective layer, thereby protecting against the dissolution of lead. However, in areas where water is soft, and the pH value may be decreased even slightly below pH=5, there is an increase of lead solubility. In these conditions water that stays in touch with pipes may even contain more than 1 mg Pb/L. According to European Union regulations, drinking water should not contain more than 0.05 mg Pb/L [3]. However, the World Health Organization (WHO) recommends a reduction of the maximum lead concentration to 0.01 mg/L. In Poland, drinking water should not contain more than 0.025 mg Pb/L (valid until 1 January 2013) and to 0.01 mg Pb/L (valid from 1 January 2013) [4].

The risk arising from the presence of heavy metals such as lead in water is associated with a lack of its biodegradation and its ability to accumulate in the environment. The toxic effect of lead on living organisms manifests itself in

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the hematopoietic system, in hem synthesis, the inhibition of haemoglobin synthesis and in shortening the lifespan of erythrocytes, leading ultimately to anaemia [5]. Lead also has a toxic action on the nervous and immune systems and impairs the functioning of the kidneys and the alimentary system [5, 6]. The degree of water toxicity varies depending on the water quality characteristics, and also varies among organisms. For this reason, removal of ionic lead form aqueous solutions is an important problem to solve.

Many interesting studies concerning physicochemical methods used to eliminate heavy metals from water and effluents have been reported in the scientific literature [7, 8]. In recent years several papers on the use of organic waste (as sorbents) for the elimination of lead ions have been written [9-12].

In spite of a good deal of research in this field, the mechanism of binding and concentrating heavy metals by sorbents of natural origin is not fully known. The process is supposed to proceed through ion exchange owing to the presence of functional groups such as carboxyl, phenyl, and hydroxyl groups [12, 13]. Also, complexation reactions are possible. In addition to chemisorption, physical adsorption, microprecipitation, and redox reactions can occur [13].

Important information concerning the mechanism of heavy metal ion binding could be the form in which they occur in the solution, which depends on their concentration and the conditions of the process environment. The sorption properties of the biomass are also important, which can be enhanced by modifying its surface by physical or chemical methods [11]. Natural sorbents are also a feedstock for the production of activated carbons [14-16].

The goal of the study was to determine and compare the sorption properties of ground walnut shells (*Juglans regia*) and plum stones (*Prunus domestica* L.) toward Pb^{2+}, and examine the effect of selected factors, such as sorbent concentration, and pH and temperature for model aqueous solution on Pb^{2+} sorption.

Experimental Procedures

Preparation of Sorbents

Walnut shells (*Juglans regia*) and plum stones (*Prunus domestica* L.) without the kernels were used for the study as natural sorbents. Washed and dried material were crushed to particle size below 0.5 mm. Before sorption, the shells and the stones were treated with 0.001 mol/L nitric acid to remove surface impurities, and then washed with reverse osmosis water until the pH attained that of pure reverse osmosis water (about 5.90), and next dried at temperatures of up to 323 K.

Sorption Process

A sorption process was performed in beakers with a relevant mass of sorbent and lead ions solutions with an initial concentration of lead from about 6.0 to 110 mg Pb/L. The lead solution was prepared from a solution of $Pb(NO_3)_2$, made by POCH Gliwice. The experiments were performed for 0.3, 0.5, 0.7, and 1.0 g of walnut shells and for 0.3, 0.5, and 1.0 g of plum stones. The volume of the solutions in the beakers was 100 mL. The pH of the studied solutions was changed from 2.0 to 5.0 at constant ionic strength equal to 0.02 mol/L. The pH was controlled with a 0.02 mol/L solution of nitric acid, while the ionic strength was controlled with a 0.04 mol/L solution of potassium nitrate(V). All solutions were prepared using reverse osmosis water.

The content of the beakers was continuously stirred with a mechanical stirrer at 120 at the constant temperature ranged from 293 to 313±0.5K. The experiments lasted for one hour (in this time the system reached equilibrium).

The lead(II) content of the solutions after adsorption was determined by flow-through coulometry using an EcaFlow 150 GLP apparatus manufactured by POL-EKO. Before measurements, the solutions were passed through a filter paper to remove solid particles. Three measurements were performed for each sample.

The amount of lead(II) ions adsorbed on the sorbent's surface was calculated from this formula:

$$Q = \frac{V(c_0 - c_k)}{m} \tag{1}$$

...where: Q – amount of the metal ions per gram of the sorbent (mg/g), V – is the volume of the solution in the flask (L); c_o and c_k – are the initial and final concentrations of lead(II) ions (mg/L); m – is the quantity of dry mass of the adsorbent (g).

Results and Discussion

The Effect of the Sorbent Concentration on the Sorption of Pb^{2+} Ions from Aqueous Solutions

The study of the sorbent's adsorption as a function of its concentration is shown in Fig. 1. The curves show that for both sorbents, the degree of removal of Pb^{2+} ions from aqueous solutions increases with rising concentrations of sorbent until reaching a maximum at a concentration of 5 g/L. In the case of walnut shells, the maximum depletion can reach 80.1%, whereas for plum stones the number is 69.5%. Hence, at the same concentration of sorbent, walnut shells are more efficient in removing Pb^{2+} from the solution.

Further increasing sorbent concentration does not cause a significant change in the degree of Pb^{2+} ions reduction. This is probably associated with the aggregation of sorbent particles in the solution. That process might restrict the access of metal ions to functional groups on the sorbent surface [17, 18]. Therefore, further studies were performed at the concentration of 5 g/L sorbent.

Effect of pH on the Sorption of Pb²⁺ Ions from Aqueous Solutions

The pH of the solution is one of the most important factors controlling the removal of heavy metals from aqueous solutions. The effect of this factor on Pb²⁺ sorption on ground walnut shells and plum stones was studied in very acidic solutions (pH 2.0-5.0).

The results obtained, shown in Fig. 2, confirm the close relationship between the pH of the solutions undergoing treatment and the efficiency of Pb²⁺ removal on the sorbents studied. For both walnut shells and plum stones, the sorption increases in pH range from 2.0 to 4.0. The sorption maximum was reached for the plum stones at pH value 4.0 (±0.1). While in solutions with pH value 5.0 (±0.1), a significant reduction in sorption was observed. This dependence for the walnut shells, when the pH value is over 4.0, requires further research and at this stage unambiguous interpretation is not possible.

Analysis of the presented dependence shows that in the highly acidic solutions and in the highly alkaline solutions sorption was decreased. Probably it is connected with a different charge on the sorbent surface. The type and size of the charge depends on pH value and functional groups on the surface of the sorbent [19]. The confirmation of the presence of functional groups (e.g. carboxyl, phenolic, and hydroxyl groups) can be IR spectra of plum stones, (for example, the spectrum shown in Fig. 3).

Characteristic bands observed at 3,423.53 cm⁻¹ and 1,425.13 cm⁻¹ are probably related to the presence of hydroxyl and amino groups. While the band at 1,744.25 cm⁻¹ originates from group C=O. A peaks in the wavenumber range from about 1,620 to 1,430 cm⁻¹, which may indicate the presence of aromatic bounds. A Peak at 559.58 cm⁻¹ may indicate the presence of S=O bounds. Although the presence of the above functional groups on the surface of the sorbents is also confirmed by literature data [18], this issue requires further study.

The pH value for which we obtained the maximum sorption capacity (in this case pH=4.0), is a so-called point of pH zero charge pHzpc [12]. When the pH value is below the pHzpc point, the surface of a sorbent is positively charged and when the pH value is above pHzpc point, the surface of a sorbent is charged negatively. A positive charge present on the surface of the sorbent may be explained, among other things, by the presence of alkaline functional groups and by excessive surface protonation [12, 19]. When a positive charged barrier is formed, the metal cations have limited access to the sorbent surface. In addition, together with a reduction of pH value, the competition of hydrogen ions for active sites on the surface of the sorbent increases. The effect of these phenomena is the reduction of sorption. On the other hand, when the surface of the sorbent has a negative charge (as a result of ionization of acid groups - mainly carboxylic, phenolic, and hydroxyl), there is an electrostatic attraction between metal ions and the sorbent surface which increases the sorption. This phenomenon is observed in the pH range in which lead appears in the form of Pb²⁺. Also, when the pH value increases, the solution contains fewer hydrogen ions that compete with Pb²⁺ for sorption, thus increasing the efficiency of Pb²⁺ sorption [12].

The pH value of the solution also determines the quality and concentration of ionic forms in solution. In strongly acidic solutions, metals exist mainly as cations. The gradual increase in pH value leads to the formation of complex ions
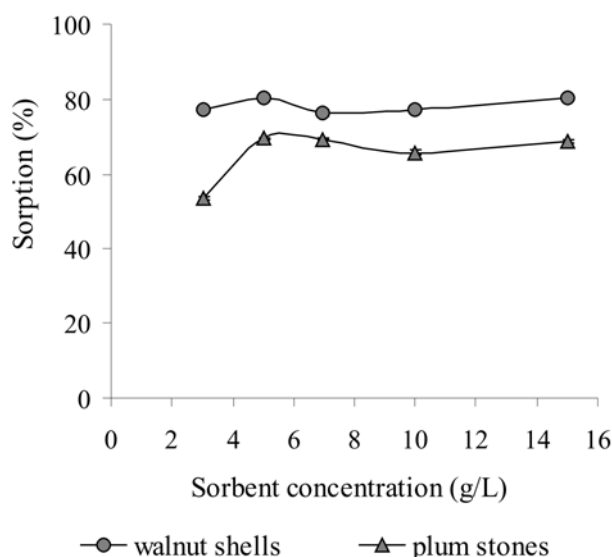

Fig. 1. The effect of the sorbent concentration on the sorption of Pb²⁺ ions on walnut shells and on plum stones (initial Pb²⁺ concentration 15.6 mg/L, pH of 4.0±0.1, sorbent particle size class <0.5 mm, ionic strength 0.02 mol/L, temperature (298±0.5) K, time of adsorption 1 h, mixing rate 120 rpm.). Uncertainty in the sorption capacity for the plum stones: 0.48, 0.29, 0.26, 0.67, 0.51%. Uncertainty in the sorption capacity for walnut shells: 0.60, 0.25, 0.84, 0.65, 0.24%.
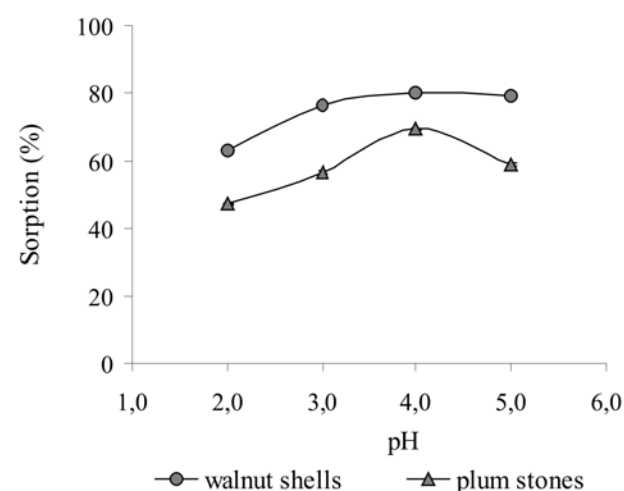

Fig. 2. The effect of pH on the sorption of Pb²⁺ ions on walnut shells and on plum stones (initial Pb²⁺ concentration 15.6 mg/L, sorbent concentration 5 g/L, sorbent particle size class <0.5 mm, ionic strength 0.02 mol/L, temperature (298±0.5) K, time of adsorption 1 h, mixing rate 120 rpm.). Uncertainty in the sorption capacity for the plum stones: 0.34, 0.50, 0.29, 0.56%. Uncertainty in the sorption capacity for walnut shells: 0.86, 0.80, 0.25, 0.62%.
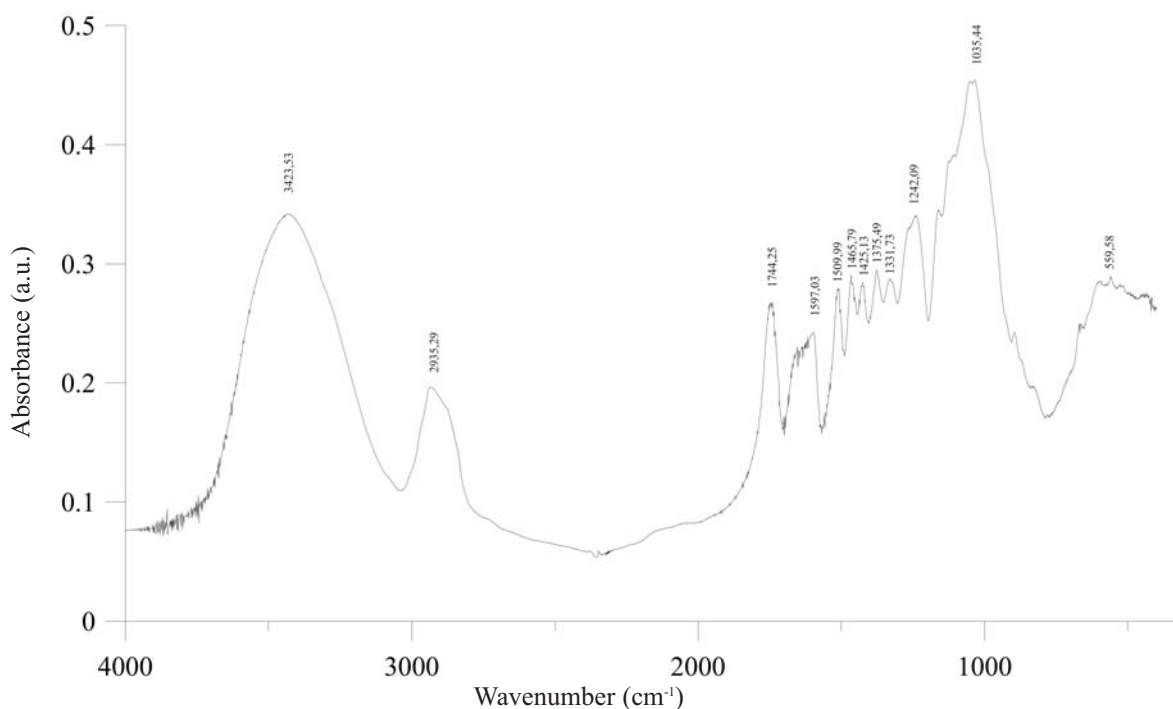
Fig. 3. IR spectra of plum stone samples.

and precipitation of metal ions in the form of hydroxide. Taking into consideration that the exponent of solubility product of $Pb(OH)_2$ is 20, it was calculated that in the starting solution with a concentration of lead equal to 15.6 mg/L, lead hydroxide is completely precipitated at pH value of about 6.0 [20]. In the case of plum stones, the sorption reduction occurring at pH=5.0 ($\pm$0.1) probably results from the formation of hydroxyl ions of lead.
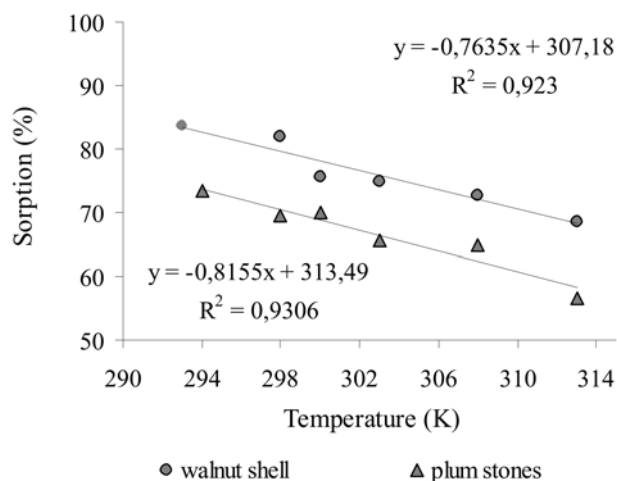

Fig. 4. The effect of temperature on the sorption of Pb^{2+} ions on walnut shells and on plum stones (initial Pb^{2+} concentration 15.6 mg/L, sorbent concentration 5 g/L, sorbent particle size class <0.5 mm; ionic strength 0.02 mol/L, pH of 4.0$\pm$0.1, time of adsorption 1 h, mixing rate 120 rpm). Uncertainty in the sorption capacity for the plum stones: 0.22, 0.30, 0.37, 0.63, 0.35, 0.31%. Uncertainty in the sorption capacity for walnut shells: 0.44, 0.34, 0.41, 0.47, 0.49, 0.75%.

The Effect of Temperature on the Sorption of Pb^{2+} Ions from Aqueous Solution

In order to study the effect of temperature on Pb^{2+} sorption on ground walnut shells and plum stones, sorption experiments were performed in the range from 293 to 313 K. Other conditions remained the same as in previous experiments.

For both sorbents it was noted that as the temperature was increased in the range from 293 to 313 K, sorption decreased (Fig. 4). Such a result confirms the exothermic nature of Pb^{2+} sorption on walnut shells and plum stones. The decrease in sorption properties in a temperature range of 293 to 313 K may result from damage to active sites on the sorbent surface or the shift of the process equilibrium toward desorption of metal ions from the surface to the solution [18].

Isotherm of Pb^{2+} Adsorption on Walnut Shells and on Plum Stones

Sorption of Pb^{2+} on the studied sorbents was described using the two most common adsorption models – the Langmuir and Freundlich isotherms. Characteristics of these models are given in Table 1.

The initial concentration of Pb^{2+} ions on the sorbents studied changed from about 6.0 to 110 mg/L. The results of the study described with the Langmuir and Freundlich equations are shown in Figs. 5 and 6.

The values of coefficients a and b in the Langmuir equation, and K and n in the Freundlich equation were determined based on the linear form of these equations

Table 1. Characteristics of adsorption isotherms [12, 21].

Isotherm	Langmuir		Freundlich	
Assumptions	Monolayer adsorption on a uniform surface		Adsorption on a non-uniform surface empirical	
Equation	$$Q = \frac{ab \cdot c_k}{(1 + b \cdot c_k)}$$	(2)	$$Q = K \cdot c_k^{1/n}$$	(4)
Linear form	$$\frac{1}{Q} = \frac{1}{ab} \cdot \left(\frac{1}{c_k} + b\right)$$	(3)	$$\log Q = \log K + \frac{1}{n} \cdot \log c_k$$	(5)

where: Q – amount of the metal ions per gram of the sorbent (mg/g), c_k – the final concentrations of lead(II) ions (mg/L), a and b – Langmuir coefficients, K and n – Freundlich coefficients

Table 2. Langmuir and Freundlich isotherm coefficients and their uncertainties obtained for walnut shells and plum stones.

	a (mg·g⁻¹)	Δa (mg·g⁻¹)	b (L·mg⁻¹)	Δb (L·mg⁻¹)	R
Langmuir isotherm	Walnut shells				
	23.1	0.53	0.03347	0.00006	0.984
	Plum stones				
	21.2	0.47	0.03346	0.00005	0.940
	K (mg¹⁻ⁿ·g⁻¹·Lⁿ)	ΔK (mg¹⁻ⁿ·g⁻¹·Lⁿ)	n	Δn	R
Freundlich isotherm	Walnut shells				
	0.95	0.02	1.36	0.01	0.985
	Plum stones				
	0.78	0.02	1.31	0.01	0.993

(Table 1) using the effective regression method [22]. All the parameters and their uncertainties were calculated using Microsoft EXCEL. The calculated values of adsorption isotherm coefficients and the correlation coefficients R are presented in Table 2.

Based on the data shown in the tables above, it is difficult to decide unequivocally which model better describes Pb²⁺ sorption on walnut (the values of R are practically the same for the tested concentrations range of lead ions). In the case of plum stones a better fit of experimental data was noted for the Freundlich isotherm.

Both isotherms provide important information about the sorbents studied and the process of Pb²⁺ sorption from aqueous solutions. Based on the value of the maximum sorption
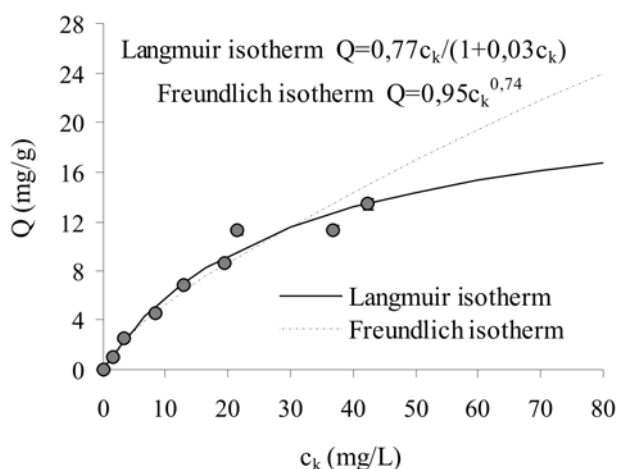

Fig. 5. Langmuir and Freundlich isotherms for Pb²⁺ adsorption on walnut shells (sorbent concentration 5 g/L, sorbent particle size class <0.5 mm, ionic strength 0.02 mol/L, pH of 4.0±0.1, temperature (298±0.5) K, time of adsorption 1 h, mixing rate 120 rpm).

Fig. 6. Langmuir and Freundlich isotherms for Pb²⁺ adsorption on plum stones (sorbent concentration 5 g/L, sorbent particle size class <0.5 mm, ionic strength 0.02 mol/L, pH of 4.0±0.1, temperature (298±0.5) K, time of adsorption 1 h, mixing rate 120 rpm).
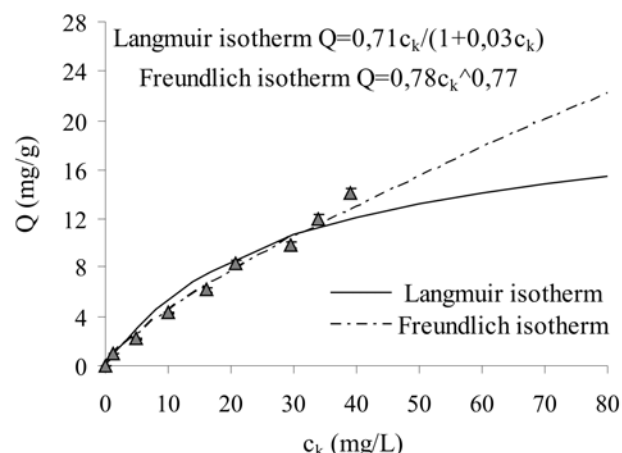
capacity (i.e. the maximum amount of metal ions needed to form a complete monolayer), which can be estimated using the Langmuir model, quantitative evaluation of the sorption process was performed based on *a* coefficient for both materials. For walnut shells, the constant has a value of 23.1 mg/g, whereas for plum stones it is 21.2 mg/g, so walnut shells show *a* slightly better sorption capacity toward Pb^{2+} ions than plum stones.

The other parameter of the Langmuir isotherm, the constant *b*, represents the energy of adsorption [12]. The lower the value of the constant *b*, the higher the affinity of the sorbent toward metal ions. In general, a good sorbent should be characterized by a low value of *b* and a high value of *a* [9].

The constants in the Freundlich isotherm also provide valuable information about the adsorption process. Parameter *K* in the Freundlich isotherm allows, among other things, assessment of the sorption capacity of the sorbent, while the constant *n* defines the intensity of adsorption [23]. The calculated value of coefficient *n* is 1.36 for walnut shells and 1.31 for plum stones; the fact that both parameters take values in the interval <1,10> demonstrates that adsorption on these sorbents is "advantageous" [12]. The lower the $1/n$ value, the greater the adsorption system's non-uniformity in terms of energy [19]. In contrast to the Langmuir model, adsorption described by the Freundlich isotherm is not limited to a monolayer.

Conclusions

1. Walnut shells and plum stones can be used to remove Pb^{2+} ions from aqueous solutions. For the tested concentrations range and process conditions in the case of walnut shells the depletion of Pb^{2+} in the solution was 62.9-83.7% and for the plum stones 47.2-81.3%.
2. Sorption of Pb^{2+} on walnut shells and plum stones depends on sorbent concentration, the pH of the solution, and temperature. In the cases of both sorbents, the optimum sorbent concentration is 5 g/L. The best sorption on walnut shells and plum stones was noted at pH 4.0±0.1. The study also showed that as the temperature increases (from 293 to 313 K), sorption gradually decreases.
3. Adsorption of Pb^{2+} on walnut shells can be described by both the Langmuir and Freundlich models (the values of *R* are very similar). In the case of plum stones, a better fit of the function to the measurement data was obtained for the Freundlich isotherm. The maximum sorption capacity of walnut shells was for 23.1 mg/g, whereas for plum stones it was 21.2 mg/g. The obtained values of the Langmuir parameter *a* support the usefulness of the studied sorbents for the removal of Pb^{2+} from aqueous solutions.

Acknowledgements

References

1. DOJLIDO J. Chemistry of surface waters. Wyd. Ekonomia i Środowisko, Bydgoszcz **1995** [In Polish].
2. MOORE J., RAMAMOORTHY J. Heavy metals in natural water. Springer-Verlag **1984**.
3. Council Directive 98/83/EC of 3 November 1998 relating to the quality of drinking water. Official Journal L 330, 0032, **1998**.
4. Regulation of Minister of Health of 29 March **2007** relating to the quality of drinking water (J.Law. 07.61.417) [In Polish].
5. SEŃCZUK W. Toxicology. Wyd. PZWL, Warszawa **1999** [In Polish].
6. RAVI RAJA A., VISHAL BABU G. N., MENEZES G., VENKATESH T. Lead Toxicity as a result of herbal medication. Indian J. Clin. Biochemistry, **23**, 200, **2008**.
7. HUANG R. C. H., TALBOT F. D. The Removal of Copper, Cadmium and Lead from Dilute Solutions using from Fractionation. Can. J. Chem. Eng., **51**, 709, **1973**.
8. CHAREWICZ W., BASAK S. Flotation of Metal Hydroxide Precipitates. J. Chem. Biotechnol., **32**, 407, **1982**.
9. GUPTA S., KUMAR D., GAUR J.P. Kinetic and isotherm modeling of lead(II) sorption onto some waste plant materials. Chem. Eng. J., **148**, 226, **2009**.
10. QI B.C., ALDRICH C. Biosorption of heavy metals from aqueous solution with tobacco dust. Bioresour. Technol., **99**, 5595, **2008**.
11. NADEEMA R., HANIF M. S., SHAHEEN F., PERVEEN S., ZAFAR M. N., TAHIRA I. Physical and chemical modification of distillery sludge for Pb(II) biosorption. J. Hazard. Mater., **150**, 335, **2008**.
12. MEENA A.K., KADIRVELU K., MISHRAA G.K., RAJAGOPAL C., NAGAR P.N. Adsorption of Pb(II) and Cd(II) metal ions from aqueous solutions by mustard husk. J. Hazard. Mater., **150**, 619, **2008**.
13. SANAK-RYDLEWSKA S. Elimination of lead ions using natural sorbents. Conference materials, Conference "Environmental management in the context of sustainable development of the industrialized areas." 20-22. 03. 2007 Szczyrk, pp.115-25, **2007** [In Polish].
14. BACCAR R., BOUZID J., FEKI M., MONTIEL A. Preparation of activated carbon from Tunisian olive-waste cakes and its application for adsorption of heavy metals ions. J. Hazard. Mater., **162**, 1522, **2009**.
15. TAJAR A. F., KAGHAZCHI T., SOLEIMANI M. Adsorption of cadmium from aqueous on sulfurized activated carbon prepared from nut shells. J. Hazard. Mater., **165**, 1159, **2009**.
16. KAZEMIPOUR M., ANSARI M., TAJROBEHKAR S., MAJDZADEH M., KERMANI H.R. Removal of lead, cadmium, zinc, and copper from industrial wastewater by carbon developed from walnut, hazelnut, almond, pistachio shell, and apricot stone. J. Hazard. Mater., **150**, 322, **2008**.
17. SARI A., TUZEN M. Biosorption of Pb(II) and Cd(II) from aqueous solution using green alga (*Ulva lactuca*) biomass. J. Hazard. Mater., **152**, 302, **2008**.
18. ULUOZLU O. D., SARI A., TUZEN M., SOYLAK M. Biosorption of Pb(II) and Cr(III) from aqueous solution by lichen (*Parmelina tiliaceae*) biomass. Bioresour. Technol., **99**, 2972, **2008**.

19. BANSAL R.Ch., GOYAL M. Activated carbon adsorption. Wyd. Naukowo-Techniczne, Warszawa **2009** [In Polish].

20. MIZERSKI W. Chemical tables. Wyd. Adamantan, Warszawa **2008** [In Polish].

21. ATKINS P.W. Physical Chemistry. Wyd. PWN, Warszawa **2007** [In Polish].

22. SZYDŁOWSKI H. Introduction to the physics lab. Wyd. UAM, Poznań **1996** [In Polish].

23. HAN R., ZHANG J., ZOU W., SHI J., LIU H. Equilibrium biosorption isotherm for lead ion on chaff. J. Hazard. Mater., **125**, 266, **2005**.