Physicochem. Probl. Miner. Process. 52(1), 2016, 380−396

www.minproc.pwr.wroc.pl/journal/

Physicochemical Problems
of Mineral Processing

ISSN 1643-1049 (print)
ISSN 2084-4735 (online)

Received April 21, 2015; reviewed; accepted July 31, 2015

REMOVAL OF Pb(II) AND Cd(II) IONS FROM AQUEOUS SOLUTIONS WITH SELECTED ORGANIC WASTES

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Abstract: The authors investigated sorption of Pb(II) and Cd(II) ions from aqueous solutions on selected natural wastes: sunflower hulls, walnut shells and plum stones. The chemical and physical structure of the surface of these sorbents was determined using infrared spectrometry and scanning electron microscopy. The most favourable physicochemical parameters of the sorption processes were also defined. The sorption of Pb(II) and Cd(II) ions was described according to the Langmuir and Freundlich models. It has been shown that the adsorbents studied can be effectively used in removing heavy metals from aqueous solutions. The sunflower hulls have the highest sorption capacity for Pb(II) and Cd(II) ions. It is equal to 36.93 mg/g for the Pb(II) ions and 19.93 mg/g Cd(II) ions. The calculated values of thermodynamic functions indicate a spontaneous ($\Delta G^o < 0$) and exothermic ($\Delta H^o < 0$) nature of the sorption processes. A participation of ion exchange in these processes is significant. Desorption tests confirm that the adsorbed heavy metals can be recovered and the sorbent materials after regeneration can be reused.

Keywords: *biosorption, Pb(II), Cd(II), organic wastes, adsorption isotherms*

Introduction

Water pollution with heavy metals is now one of the most important environmental threats. These metals have harmful effects on living organisms, which are related to their carcinogenic and mutagenic properties and the ability of the metals to bioaccumulation (Senczuk, 1999).

For water and waste water purification from heavy metals a number of conventional methods are used, such as chemical precipitation (Alvarez et al., 2007; Ghosh et al., 2011), ion exchange (Kocaoba, 2007; Rao et al., 2010) and adsorption on active carbon (Sulaymon et al., 2009; Tajar et al., 2009; Machida et al., 2012). The methods are widespread and have many advantages. However, due to their limitations

http://dx.doi.org/10.5277/ppmp160132

and high cost of application (especially in low concentration of contaminants) they also have some disadvantages. Therefore, new alternatives that will combine efficiency with economy should be searched for. Natural sorbents give perspectives to meet those requirements. Among them both dead organic matter and living micro-organisms may be mentioned. Sorption capacity of this type of organic materials to heavy metals ions is significant, which was lately confirmed, e.g. by Qi and Aldrich (2008), Sari and Tuzen (2008), Uluozlu et al. (2008), Gupta et al. (2009), Saeed et al. (2009), Azouaou et al. (2010), Blazquez et al. (2011).

The aim of the study was to experimentally confirm the possibility of using organic waste, such as sunflower hulls, walnut shells and plum stones, for the removal of Pb(II) and Cd(II) ions from aqueous solutions in single-component systems. The influence of selected physical and chemical parameters of organic materials on the sorption processes has been determined and the possibility of their regenerating examined. Other investigations conducted to elucidate the mechanism of binding heavy metals from solutions involved determining the chemical and physical structure of the organics used. The sorption processes have been described using well-known models of sorption and the maximum sorption capacity of the materials tested has been calculated.

Materials and methods

Three natural sorbents were used in the study: sunflower (*Helianthus L.*) hulls, walnut (*Juglans regia L.*) shells and plum (*Prunus domestica L.*) stones, the latter free from seeds. The material was washed, dried, ground and sieved to obtain the grain fraction below 0.5 mm (fraction was selected based on results obtained in earlier studies). Then it was purified by treating with 10^{-3}M nitric and hydrochloric acids solutions, followed by washing with reverse osmosis water until the pH attained that of the pure reverse osmosis water, i.e., about 6.0, and then dried at 323K.

Sorption experiments were performed in beakers containing 100 cm^3 of a test solution into which known weights of the sorbent (sample weights: 0.3, 0.5, 0.7, 1.0 and 1.5 g) were added. The initial Pb(II) and Cd(II) ion concentrations ranged from 6.3 mg/dm^3 to 109.4 mg/dm^3. Metals were added as the water solutions of $Pb(NO_3)_2$ and $Cd(NO_3)_2$ $4H_2O$ (p.p.a.). All the experiments run at a constant ionic strength of 0.02 mol/dm^3, which was adjusted with a solution of KNO_3 at a concentration of 0.04M. The range of initial pH of the test solutions was from 2.0 to 5.0 (± 0.1) (its value was adjusted with 0.1M HNO_3).

All the solutions with the sorbents added were continuously stirred for one hour (in this time the system reached equilibrium) with a mechanical stirrer at 120 rpm at the constant temperature 298±0.5 K. In addition, the studies of a temperature effect were conducted in the range 293-313±0.5 K (Bozecka, 2013).

The desorption process was studied for the sunflower hulls and walnut shells used earlier to remove Pb(II) and Cd(II) ion from the solutions whose initial concentrations of Pb and Cd were 15.6 mg/dm^3. The sorbents were regenerated with 50 cm^3 0.2M solutions of HNO_3 or HCl. The experimental conditions were the same as in the case of the sorption process. The progress of the desorption effectiveness was determined after 15, 30, 45 and 60 minutes of the tests.

The final concentration of Pb(II) and Cd(II) ions in a solution after sorption and regeneration was determined by the flow coulometry method using an EcaFlow 150 GLP (POL-EKO, Poland). Before the measurements, all the samples were filtered to remove solid particles. Three measurements were performed for each sample. The values of equilibrium concentrations shown in Tables 1-4 are arithmetic averages.

The sorption capacity was calculated from the formula presented below:

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

where: Q –content of the Cd(II) ions in the sorbent (mg/g); V – the volume of the solution (dm^3); c_o and c_{eq} – the initial and final concentrations of Cd(II) ions (mg/dm^3); m – the dry mass of the adsorbent (g).

Identification of surface functional groups was carried out using infrared absorption spectra recorded with BIO-RAD FTIR spectrometer (model FTS-165) for the samples prior to and after sorption (each sample had an initial concentration of 109.4 mg/dm^3 of Pb or Cd cations). The frequency range was 4000-400 cm^{-1} and a resolution 4 cm^{-1}. The pellets were made from a mixture of a dried sorbent and the spectrally pure potassium bromide (at the ratio 1:400) pressed at 10 MPa.

The morphology of the selected organic sorbents was determined using a scanning electron microscope FEI Quanta 200 FEG. The analyses were supplemented by microchemical assays using an EDS spectrometer. The tests were carried out on starting (i.e. untreated) samples and on the samples after the sorption process.

Results and discussion

Determination of the chemical and physical structure of the sorbents

The surface morphology images of the sorbents prior to and after the sorption process and the corresponding EDS spectra (Figs 1(a-f) and 2(a-h), respectively) show that lead and the cadmium are below detection limits in the starting materials.

Both elements are present on the surface of the samples used in the sorption tests (Fig. 2a-h), but there are no traces of microprecipitated Pb and Cd compounds. In some areas, however, there are indications of the sorption involving mainly the ion exchange mechanism (e.g. Fig. 2a, c and e). Distribution of adsorbates on the surface is random, which may indicate their heterogeneity (Bozecka, 2013; Bozecka et al., 2014a).

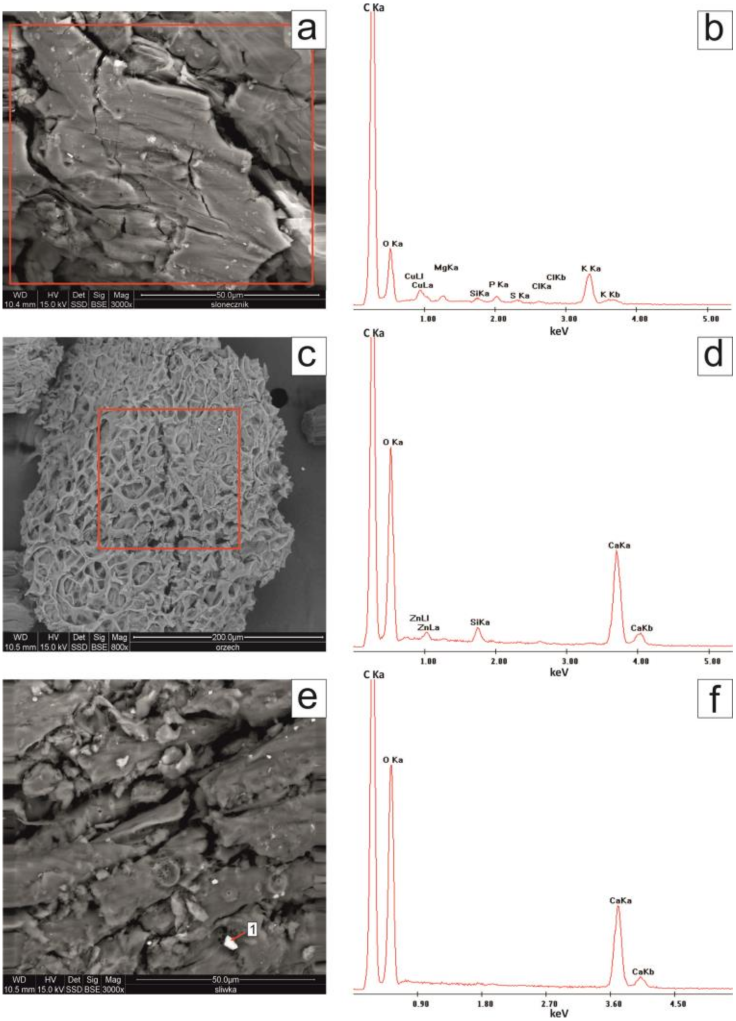

Fig. 1. Examples of SEM images with EDS spectra obtained for samples of starting sunflower hulls (a, b), walnut shells (c, d) and plum stones (e, f) (Bozecka, 2013; Bozecka et al., 2014a)

The presence of functional groups in the starting samples can be traced in the IR spectra (Fig. 3). They show strong absorption bands at approximately 3420 cm^{-1}, which can be attributed to stretching vibrations of the OH groups present in alcohols and phenols or to intramolecular hydrogen bonds of carbohydrates, present in organic compounds (presumably cellulose, hemicellulose and lignin). The bands occurring in all the tested materials in the range of approximately 2930–2840 cm^{-1} can probably be related to the CH stretching vibrations of alkyl groups.

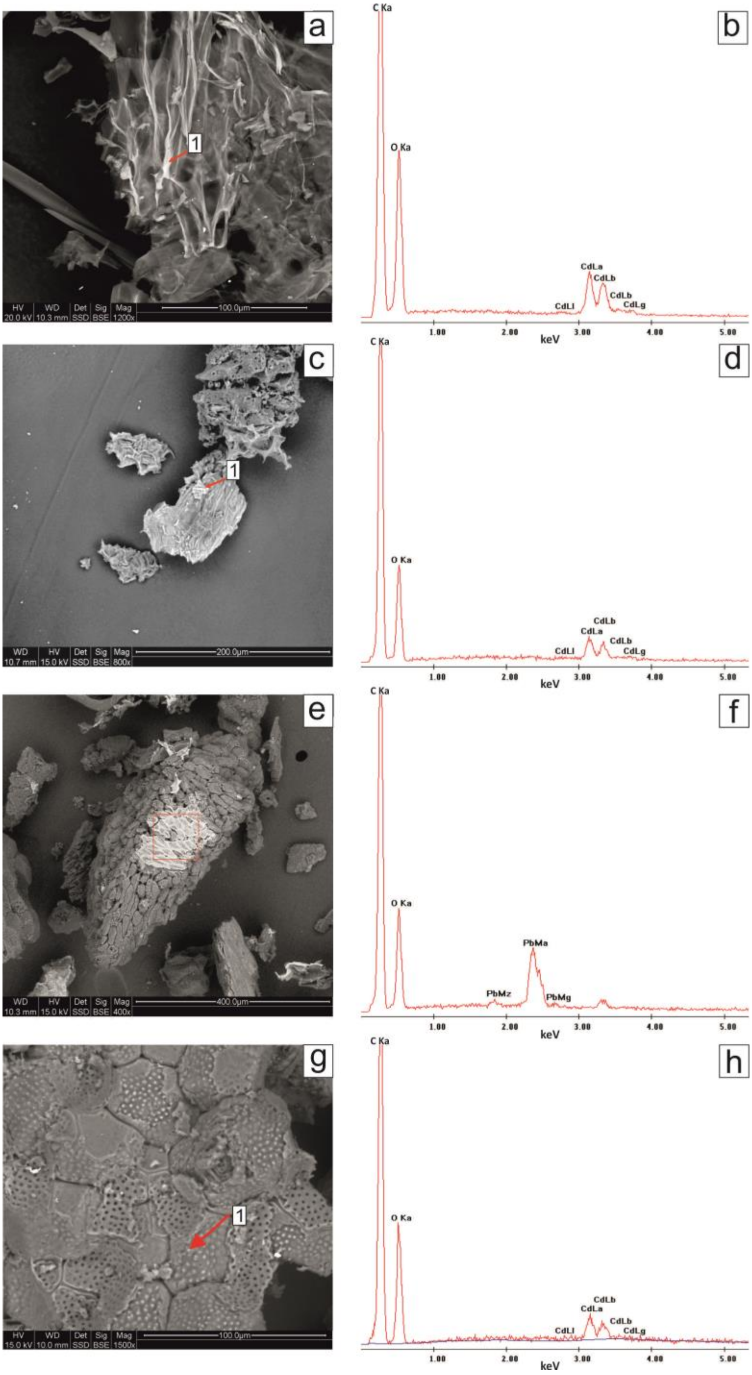

Fig. 2. Examples of SEM images with spectra EDS obtained for samples of sunflower hulls (a, b), walnut shells (c, d) and plum stones (e-h) after sorption of the Pb(II) and Cd(II) ions (Bozecka, 2013; Bozecka et al., 2014a)

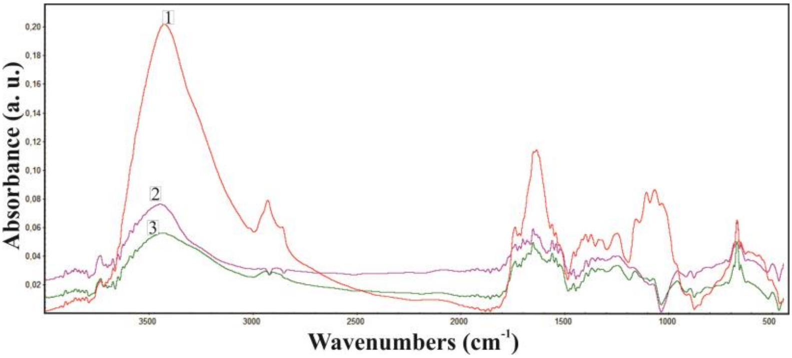

Fig. 3. Comparison of the IR spectra of starting samples of sunflower hulls (1), walnut shells (2) and plum stones (3) (after Bozecka, 2013; Bozecka et al., 2014a, b)

Another band, pronounced mainly in the walnut shells and plum stones at approximately 1740 cm^{-1} may be attributed to the vibrations of C=O carbonyl compounds (carboxylic compounds, esters, ketones, aldehydes, etc.). The presence of the esters, alcohols and phenols is also indicated by the bands in the range 1300-1000 cm^{-1} interpreted as the stretching vibrations of C-O groups.

The bands in the region of approximately 1650 cm^{-1} may be attributed to the stretching vibration of C=O groups and the bending vibration of the N-H amide group. The amines manifests their presence by the band in the range approximately 1650-1580 cm^{-1}, also attributed to the N-H bending.

Absorption in the range approximately 1600–1400 cm^{-1} indicates probably the presence of aromatic compounds. In addition, the bands between 900 and 675 cm^{-1} may be interpreted also as aromatic bands resulting from the bending vibrations out of the plane of the C–H (Uluozlu et al., 2008; Azouaou et al., 2010; Bozecka, 2013; Bozęcka et al., 2014a; Bozecka et al., 2014b).

The effects of the functional groups mentioned above on the sorption mechanism of Pb(II) and Cd(II) ions have been interpreted on the IR spectra of the samples after the sorption (Figure 4a, b, c). The intensity of all the characteristic absorption bands, including those of the OH groups (alcohols, phenols, carboxylic acids), C = O (carboxylic compounds, esters, ketones, aldehydes, etc.), and amino and amide groups decreased (Figure 4 a, b, c). Such a distinct intensity reduction occurring at all band frequencies may indicate an adhesion of the Pb(II) and Cd(II) ions that block the access to organic groups.

The strongest change in the band intensity is observed at approximately 3420 cm^{-1} for the sunflower hulls (Fig. 4a). Therefore, it can be concluded that this material is the most efficient sorbent of Pb(II) and Cd(II) ions assuming that the O–H groups are involved in the investigated sorption process. Such a conclusion is consistent with the results discussed in Section 3.2.4, which demonstrate that the sunflower hulls in comparison with other materials have the highest relative capability to remove cations.

Apart from the O–H groups, the carbonyl group C=O (carboxylic compounds, esters, ketones, aldehydes, etc.) and the amine or amide groups may also play an important role in the sorption of Pb(II) and Cd(II) ions. A significant intensity reduction of the bands at the frequencies characteristic of these organic groups may point to their blocking by the Pb(II) and Cd(II) ions adsorbed from the solution. The spectra also confirm that the sorption processes also involve the ion exchange mechanism (Bozecka, 2013; Bozecka et al., 2014a, b).

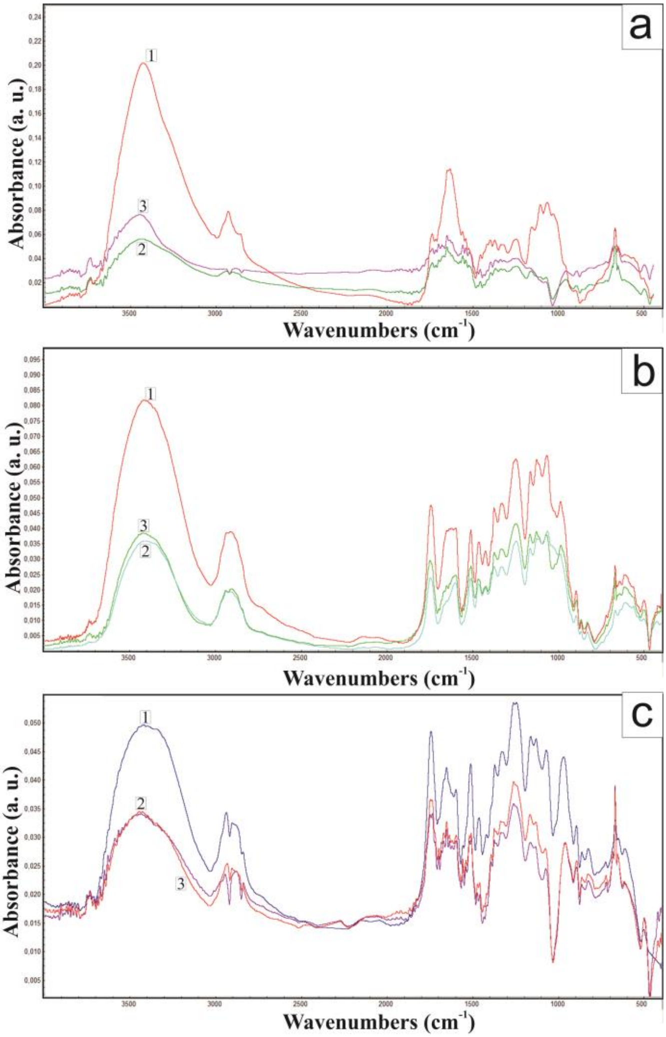

Fig. 4. Comparison of IR spectra obtained for sunflower hulls (a), walnut shells (b) and of plum stones (c) prior to (1) and after sorption of Pb(II) (2) or Cd(II) (3) ions (Bozecka, 2013; Bozecka et al., 2014a, b)

Sorption process of Pb(II) and Cd(II) ions from aqueous solutions

Impact of sorbent mass

Sorption was measured in the samples with the mass 0.3, 0.5, 0.7, 1.0 and 1.5 g (Fig. 5). All the sorbents remove from aqueous solutions an increasing amount of the Pb(II) and Cd(II) ions with an increasing weight of the sample until a maximum sorption at a sorbent mass of 0.5 g is reached. A further increase of the sorbent mass does not significantly affect the amount of the ions adsorbed. Presumably, it is associated with sorbent particle aggregation in the solution, which can reduce an access of the cations to the surface active centres of the sorbent (Uluozlu et al., 2008; Gala (Bozecka) and Sanak-Rydlewska, 2011; Bozecka, 2013; Bozecka and Sanak-Rydlewska, 2011, 2015).

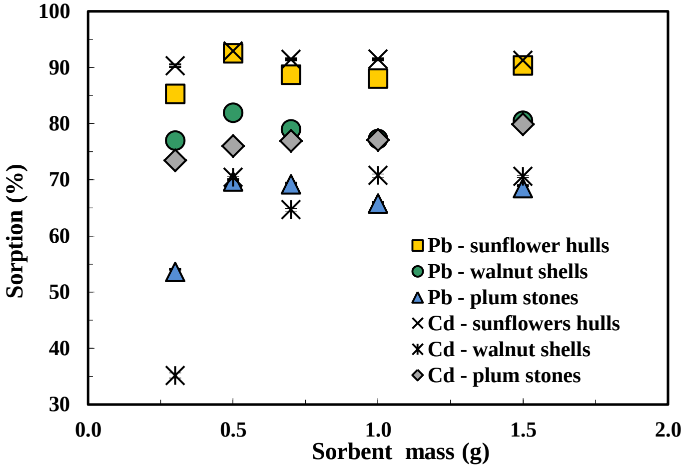

Fig. 5. The influence of the sorbent mass on sorption of the Pb(II) and Cd(II) ions on sunflower hulls, walnut shells and plum stones (c_o = 15.63 mg/dm^3; pH 4.0±0.1; sorbent's particle size class < 0.5 mm; ionic strength 0.02 mol/dm^3; temperature (298±0.5) K; time of sorption 1 h; mixing speed 120 rpm) (Bozecka, 2013)

Impact of initial pH of solutions

The sorption of the Pb(II) and Cd(II) ions in the function of the initial pH of the solution was tested for the pH values 2.0, 3.0, 4.0 and 5.0 (Fig 6).

The efficiency of sorption of the Pb(II) and Cd(II) ions by all the materials increases with the pH until it reaches a maximum in the solutions with pH of about 4.0. At pH higher than 5.0 a sorption efficiency noticeably decreases. Only is a little weaker the sorption efficiency of the Pb(II) ions on the walnut shells and sunflower hulls, but its reason is not currently possible for a clear interpretation.

The reduction in the sorption efficiency, both below and above pH of 4.0, is most likely associated with an electrostatic charge accumulated on the surface of the sorbents. The type and amount of this charge depends on the pH of the solution and on the functional groups on the surface of sorbents (Bansal and Goyal, 2009; Gala (Bozecka) and Sanak-Rydlewska, 2011; Bozecka, 2013; Bozecka and Sanak-Rydlewska, 2011, 2015).

The initial pH of the solution determines the form of the Pb and Cd ions in the solution. In a strongly acidic solution, lead and cadmium are mainly in the form of cations. The gradual increase of the pH leads to the formation of complex ions, followed by precipitation of $Pb(OH)_2$ and $Cd(OH)_2$.

Studying the effect of the solution pH on sorption of the Pb(II) and Cd(II) ions, the differences between the starting and the equilibrium pH values were noted. For example, in case of the sunflower hulls and Pb(II) ions the starting pH was 2.08, 3.04, 4.00 and 4.98, while after sorption the values were 2.78, 4.45, 5.23, and 5.34, respectively.

The sorption, hydrolysis and ionization processes explain the changes in pH. The equations 1 and 2, showing the hydrolysis degree of the Pb(II) and Cd(II) ions, indicate that at the time of their attachment to the surface of a sorbent the reaction equilibrium moves to the left. This leads to a reduction of protons in the solution and a pH increase. With the increase of the starting pH value (up to value of zero point charge – pH_{zpc}), the sorption capacity increases and the pH reaches an equilibrium state

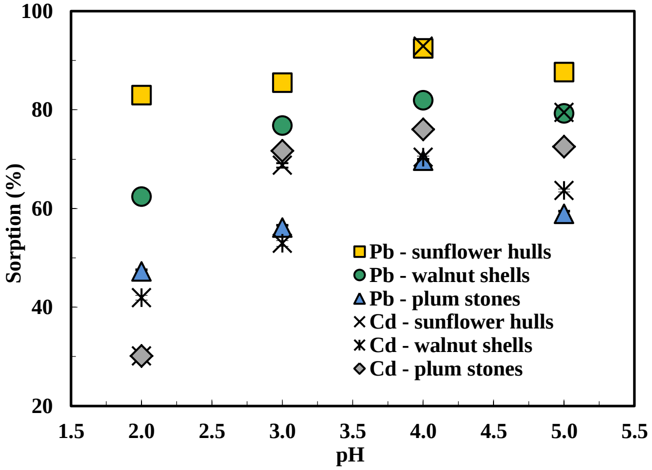

Fig. 6. The effect of pH on sorption of the Pb(II) and Cd(II) ions on sunflower hulls, walnut shells and plum stones (c_o = 15.63 mg/dm^3; sorbent mass 0.5 g; sorbent's particle size class < 0.5 mm; ionic strength 0.02 mol/dm^3; temperature (298±0.5)K; time of sorption 1 h; mixing speed 120 rpm) (Bozecka, 2013)

As soon as the $Pb(OH)^+$ or $Cd(OH)^+$ ions are adsorbed, the reaction equilibrium moves to the right, thereby increasing the concentration of protons and acidifying the solution:

$$Pb^{2+} + H_2O \leftrightarrow Pb(OH)^{+} + H^{+} \tag{1}$$

$$Cd^{2+} + H_2O \leftrightarrow Cd(OH)^{+} + H^{+} \tag{2}$$

As mentioned before, the Pb(II) and Cd(II) ions in water are subject to hydrolysis and complexation, thus the protons generated increase the acidity of the solutions. They may also be acidified as a result of hydrolysis and ionization of the functional groups present on the surface of the sorbents. However, the impact of these processes appears to be insignificant and can be ignored (Bozecka, 2013).

Impact of solution temperature

An impact of temperature on the sorption process of the Pb(II) and Cd(II) ions was tested between 293K and 313K. Other conditions were the same as in the previous series.

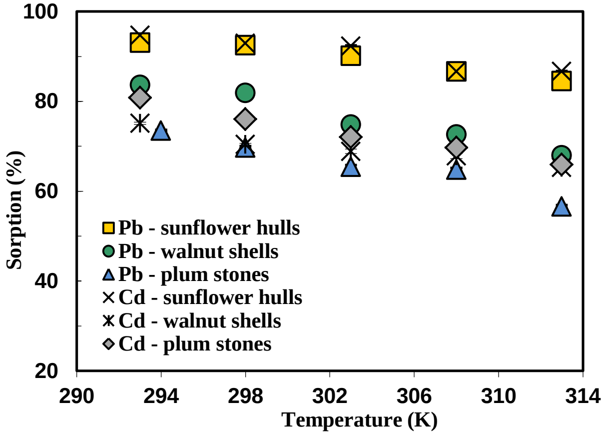

Fig. 7. The impact of the temperature on sorption of the Pb(II) and Cd(II) ions by sunflower hulls, walnut shells and plum stones (c_o = 15.63 mg/dm^3; sorbent mass 0.5 g; sorbent's particle size class < 0.5 mm; ionic strength 0.02 mol/dm^3; pH of 4.0±0.1; time of sorption 1 h; mixing speed 120 rpm) (Bozecka, 2013)

An increase of the temperature reduced sorption of the Pb(II) and Cd(II) ions (Fig. 7). This indicates the exothermic nature of the processes investigated. The decline in a sorption efficiency may be due to a destruction of the active sites present on the surface of the sorbents or shifting the equilibrium in favour of desorption of the Pb(II) and Cd(II) ions from the surface to a solution (Uluozlu et al., 2008). At higher temperatures, the kinetic energy of the adsorbed molecules increases, which may hinder their connection to the surface (Gala (Bozecka) and Sanak-Rydlewska, 2011; Bozecka, 2013; Bozecka and Sanak-Rydlewska, 2011; 2015).

Based on the experimental data and known thermodynamic relations, the changes of the standard free energy (ΔG^o), standard enthalpy (ΔH^o) and standard entropy (ΔS^o)

have been calculated using the following equation (Meena et al., 2008; Uluozlu et al., 2008; Bozecka, 2013)

$$\Delta G^{o} = -RT \ln K_c' \qquad (2)$$

where: R – ideal gas constant (8.314 10^{-3} kJ/mol K), T – temperature (K), K_c' – equilibrium constant, defined as the ratio of the concentration of metal ions on the sorbent c_a, to the concentration of ions in the solution c_{eq}, after reaching equilibrium of the sorption process.

The K_c' constant was determined for the lowest, experimental concentration of the metal (Han et al., 2005):

$$\Delta G^{o} = \Delta H^{o} - T\Delta S^{o} \qquad (3)$$

$$\ln K_c' = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT} \,. \qquad (4)$$

The change of the standard free energy (ΔG^o) was calculated from the equation 3. For all the investigated samples and in the whole range of the selected temperatures, the calculated ΔG^o is characterized by negative values (Table 1), which proves that the process is spontaneous.

The changes of standard enthalpy and entropy of the system were determined based on Eq. 4, plotting the K_c' graphs as a function of 1/T (Fig. 8). The values of ΔH^o and ΔS^o were determined from the slope and intersection of the y-axis by the linear graphs.

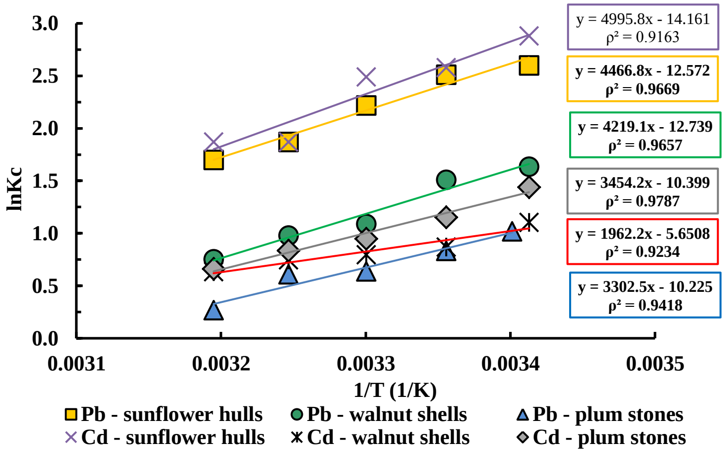

Fig. 8. Relationship between ln K_c' and 1/T for sorption of the Pb(II) and Cd(II) ions on the sunflower hulls, walnut shells and plum stones (after Bozecka, 2013)

The calculated change of the standard enthalpy (ΔH^{o}) in the systems studied reaches negative values (Table 1), confirming the exothermic nature of the process. When $\Delta H^{o}<0$, the dependence ln K_c' = f(1/T) is an increasing function (a > 0), i.e. with an increasing temperature both the sorption and the value of the equilibrium constant decrease (Fig. 5).

The changes of the standard entropy (ΔS^{o}) of the systems also have negative values (Table 1). The molecules in the adsorbed state have less freedom degrees than those in the solution, which results in a decrease of entropy (Bozecka, 2013).

Table 1. Thermodynamic functions describing the sorption of Pb(II) and Cd(II) ions from aqueous solutions by sunflower hulls (S), walnut shells (O) and plum stones (P) (Bozecka, 2013)

Function (kJ/mol)	Materials	Temperature (K)											
		293	298	300	303	308	313	293	298	300	303	308	313
		Pb(II)						Cd(II)					
ΔG^{o}	S	–6.33	–6.22	–5.58	–4.79	–4.42	–6.33	–7.01	–6.38	–5.90	–4.78	–4.87	–7.01
	O	–3.98	–3.74	–2.74	–2.50	–1.96	–3.98	–2.69	–2.15	–2.00	–1.91	–1.65	–2.69
	P	–2.49	–2.06	–1.61	–1.56	–0.69	–2.49	–3.51	–2.86	–2.39	–2.14	–1.72	–3.51
ΔH^{o}	S	–37.14						–41.62					
	O	–35.08						–16.30					
	P	–27.46						–28.72					
ΔS^{o}	S	–0.10						–0.12					
	O	–0.11						–0.05					
	P	–0.09						–0.09					

A description of the sorption of Pb(II) and Cd(II) ions with selected adsorption models

To evaluate the maximum sorption capacity of the sorbents studied toward the Pb(II) and Cd(II) ions, the authors applied commonly used adsorption models of Langmuir and Freundlich.

The Langmuir theory assumes that the surface of the adsorbent is homogeneous. Adsorption in the system is located, which means that the molecule cannot move freely across the surface. Lateral interactions between the adsorbed molecules are irrelevant. It is, therefore, a monolayer adsorption (Bansal and Goyal, 2009). The Langmuir model is described by the following equation:

$$Q=\frac{q_{\max}b\cdot c_{eq}}{(1+b\cdot c_{eq})} \tag{5}$$

where: q_{max} (mg/g) and b (dm^3/mg) are the Langmuir constants.

The parameter q_{max} is the maximum sorption capacity of the sorbent, i.e. the maximum amount of cations needed to form a complete monolayer (Han et al., 2005).

The constant *b* represents the energy of adsorption. This parameter is very useful, because it determines the sorbents affinity toward the substances removed. The higher the value of the constant *b*, the higher the affinity of the sorbent towards cations and the steeper the Langmuir isotherm. In general, a good sorbent should be characterised by high values of both the constants q_{max} and *b* (Meena et al., 2008).

The values of the coefficients q_{max} and *b* in the Langmuir equation were determined based on they linear form:

$$\frac{1}{Q}=\frac{1}{q_{\max}b}\cdot\left(\frac{1}{c_{eq}}+b\right). \tag{6}$$

The Freundlich equation has an experimental nature, well describing the adsorption on heterogeneous surfaces and microporous adsorbents. The Freundlich model is described by the following equation:

$$Q=K\cdot c_{eq}{}^{1/n} \tag{7}$$

where *K* and *n* are the Freundlich constants.

The Freundlich parameter *K* allows the assessment of the maximum sorption capacity of the sorbent and the parameter *n* is defined as the affinity constant or the binding strength. The smaller the value of *1/n*, the greater heterogeneity energy of an adsorption system (Bansal and Goyal, 2009).

To calculate the constants *K* and *n* of the Freundlich equation, the logarithmic form of this equation is used:

$$\log Q=\log K+\frac{1}{n}\cdot\log c_{eq}. \tag{8}$$

The resulting values of the coefficients of the Langmuir and the Freundlich isotherms together with their uncertainties and correlation coefficients ρ are summarized in Tables 2 and 3.

The values of the Langmuir and Freundlich constants confirm that of the three materials studied the sunflower hulls is the best sorbent for removing the Pb(II) and Cd(II) ions from water solutions. It is characterized by the highest values of the parameter q_{max} that expresses the capacity of the monolayer; the parameter *b* that determines its affinity for removing ions and for the constant *K*. The coefficient *n* in the Freundlich isotherm for all the materials is in the range from 1 to 10. That proves that the sorption processes investigated are "beneficial" (Meena et al., 2008; Gala (Bozecka) and Sanak-Rydlewska, 2011; Bozecka, 2013; Bozecka and Sanak-Rydlewska, 2011; 2015).

Table 2. Coefficients of the Langmuir isotherm and the uncertainty resulting for sorption of the Pb(II) and Cd(II) ions on sunflower hulls (S), walnut shells (O) and the plum stones (P) (Bożęcka, 2013)

Cation	Materials	q_{max} (mg/g)	Δq_{max} (mg/g)	b (dm^3/mg)	Δb (dm^3/mg)	P
Pb(II)	S	36.93	0.76	0.1512	0.0002	0.9740
	O	23.08	0.52	0.03343	0.00006	0.9837
	P	21.23	0.47	0.03457	0.00005	0.9796
Cd(II)	S	19.93	0.51	0.2264	0.0002	0.9869
	O	17.17	0.54	0.03272	0.00008	0.9485
	P	17.98	0.39	0.0777	0.0001	0.9613

Table 3. Coefficients of the Freundlich isotherm and the uncertainty resulting for sorption of the Pb(II) and Cd(II) ions on sunflower hulls (S), walnut shells (O) and the plum stones (P) (Bozecka, 2013)

Cation	Materials	K (dm^3/mg)	ΔK (dm^3/mg)	n	Δn	ρ
Pb(II)	S	4.43	0.06	1.35	0.02	0.9467
	O	0.95	0.02	1.36	0.01	0.9860
	P	0.78	0.02	1.31	0.01	0.9936
Cd(II)	S	3.10	0.04	1.60	0.02	0.9627
	O	1.22	0.02	1.82	0.02	0.9831
	P	1.27	0.02	1.44	0.01	0.9813

Sorption capacity of tested materials in relation to the lead and cadmium ions are comparable to other organic and inorganic sorbents (Bozecka, 2013; Gupta et al., 2009).

Equilibrium study on desorption of the Pb(II) and Cd(II) ions

The desorption process was studied on two sorbents, namely sunflower hulls and walnut shells, using the 0.2M solutions of nitric(V) and hydrochloric acids. The results are summarized in Table 4.

Desorption of the Pb(II) and Cd(II) ions from the surface of the two natural sorbents proceeds relatively fast. The desorption equilibrium in almost all cases was reached after 30 minutes. An extension of the desorption time practically does not significantly affect the recovery of lead and cadmium.

A comparison of the desorption efficiencies indicates that HNO_3 is more effective for the Pb(II) ions and sunflower hulls. For walnut shells there are no significant differences between the results. For both acids the desorption efficiency is high and approximates 94%.

The Pb(II) ions are desorbed more efficiently from the surfaces of sunflower hulls in comparison to walnut shells.

Table 4. Desorption of the Pb(II) and Cd(II) ions from the surface of sunflower hulls and walnut shells using nitric(V) and hydrochloric acids depending on the duration of the process

Regenerator	Materials	Regeneration time (min)							
		15	30	45	60	15	30	45	60
		Desorption (%)							
		Pb(II)				Cd(II)			
0.2 M HNO_3	S	79.49	83.36	84.56	84.61	45.41	49.21	49.23	51.03
	O	90.54	93.04	92.53	93.37	39.06	41.73	41.89	42.28
0.2 M HCl	S	68.11	69.33	69.45	69.33	64.53	65.87	67.08	68.08
	O	90.24	91.42	94.40	94.02	36.94	39.17	39.66	39.78

The recovery of cadmium is much lower than that of lead. It is 68.08% for HCl and 51.03% for HNO_3 in case of sunflower hulls and 39.78% for HCl and 42.28% for HNO_3 in the case of walnut shells. Desorption of the Cd(II) ions from sunflower hulls is more efficient than that from walnut shells.

The results confirm that protons in the solutions at $pH<2.0$ have a greater ability to attach to the sorbent surface groups than the cations of a heavy metal (Bozecka, 2013)

Conclusions

1. Sunflower hulls, walnut shells and plum stones can be effectively used for the removal of heavy metals ions from water and underpin for further research.
2. Sorption capacity of this materials in relation to the lead and cadmium ions are comparable to other organic and inorganic sorbents (Bozecka, 2013; Gupta et al., 2009).
3. Used sorption method have many advantages, which include: low cost both of purchasing and of process itself and management possibility of unwanted waste, which storage is a major environmental problem. Another advantage of used method is reusability of studied materials as well as the recovery possibility of adsorbed heavy metals.
4. Ion exchange processes are dependent on the surface construction of the sorbents used and also on the ionic radius of a metal considered
5. The best sorption properties have been revealed by sunflower hulls. In their case q_{max} was 36.93 mg/g for the Pb(II) ions and 19.93 mg/g for the Cd(II) ions.
6. The microchemical analysis indicates that lead and cadmium are not present in the starting sorbent samples. No traces of microprecipitation of lead and cadmium were observed in scanning images. In turn, there are several areas that confirm that the sorption processes involve mainly the ion exchange mechanism.
7. Among the surface functional groups, the -OH group (from alcohols, phenols, carboxylic acids), the carbonyl group C=O (from carboxylic compounds, esters, ketones, aldehydes etc.) and the amine or amide groups have been found to dominate.

8. The calculated values of thermodynamic functions indicate the spontaneous ($\Delta G^o < 0$) and exothermic ($\Delta H^o < 0$) nature of the sorption and desorption processes on the organic sorbents studied.

9. After their acid regeneration, the sunflower hulls and walnut shells can be used again to remove the Pb(II) and Cd(II) ions from aqueous solutions.

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