TOMÁŠ BAKALÁR[1], HENRIETA PAVOLOVÁ[1]

APPLICATION OF ORGANIC WASTE
FOR ADSORPTION OF Zn(II) AND Cd(II) IONS

Biosorption of Zn(II) and Cd(II) ions from aqueous solutions onto organic waste – orange peel, hazelnut shell, and walnut shell was studied using batch adsorption experiments. In the biosorption studies, equilibrium metal ion concentration was determined. Experimental data obtained were analysed in terms of Freundlich, Langmuir, Temkin, Dubinin–Radushkevich, Redlich–Peterson, Sips, Toth, and Khan isotherms. The results of the study showed that orange peel, hazelnut shell, and walnut shell can be adequately used as low-cost alternatives for the removal of Zn(II) and Cd(II) ions from aqueous solutions with maximum sorption capacities of 15.51 and 19.8 mg/g, 11.55 and 16.65 mg/g, and 26.60 and 21.10 mg/g, respectively. The highest removal efficiency of Zn(II) and Cd(II) ions was obtained for hazelnut shells. The process was fast and about 90% of metal ions were removed by all the studied biosorbents. The sorption process was possibly chemisorption occurring on a heterogeneous surface.

1. INTRODUCTION

The quality of water is affected not only by its cycle but also by a human using it in a variety of technological processes in the industry, ore processing, electronic and chemical production, etc. All of these may introduce toxic metals into water. Toxic metals are the pollutants difficult to remove when deposited in the environment. Even in low concentrations, they can be toxic. For this reason, it is necessary to handle them before they could be discharged into the environment. Various methods are used for their removal, e.g., precipitation, oxidation, reduction, biological processes, membrane filtration, adsorption, ion exchange, etc. The efficiency of each method depends on many factors. This paper presents the results of biosorption study of orange peel, walnut and hazelnut shell for removal of Zn(II) and Cd(II) ions from aqueous solutions in batch

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[1]Technical University of Košice, Faculty of Mining, Ecology, Process Control and Geotechnologies, Institute of Earth Resources, Letná 9, 042 00 Košice, Slovakia, corresponding author T. Bakalár, e-mail address: tomas.bakalar@tuke.sk

experiments. Nowadays, organic waste as a low-cost adsorbent for toxic metal removal is often used. It is feasible due to its availability, cost effectiveness, applicability, etc. It is assumed that each area differs in the quality of oranges and nuts thus the quality of their residues is also different. For this reason, locally available oranges and nuts were tested, as a low-cost source of orange peel and nutshell with minimum necessary expenses, for removal of Zn(II) and Cd(II) ions from water which can also be applied in industrial processes and wastewater treatment.

75% of the total harvested citrus fruits are orange. Orange peel is an agricultural waste (production of orange juice), which is inexpensive, readily available and in large amounts. Nevertheless, this waste is a serious environmental problem [1]. Orange peel is composed primarily of cellulose, pectin, hemicellulose, lignin, chlorophyll pigments and other low molecular compounds comprising limonene. As active sites which bind heavy metals are foreseen functional hydroxyl and carboxyl groups in cellulose [1, 2]. It is assumed that the locally obtained orange peel and nutshell material can be suitable for removal of Zn(II) and Cd(II) ions from water depending on both the experimental setup and the nature of the system used in the experiments and the results reported in the study and other studies as mentioned below.

Pérez-Marín et al. [3] studied the influence of pH on the adsorption equilibrium of Cd(II) on an orange peel. The maximum sorption capacity of orange waste was 44.96, 46.09 and 48.34 mg/g for pH 4, 5 and 6, respectively. The Sips adsorption isotherm fitted the experimental data best from Langmuir, Freundlich, Sips, and Redlich–Peterson isotherms. Annadurai et al. [4] studied the adsorption of Zn(II) on an orange peel. The maximum sorption capacity of orange peel was 5.25 mg/g at pH 7.5.

Walnut and hazelnut shells are common agricultural by-products. The main growers of these crops are Argentina – walnut and Turkey – hazelnut [5]. Several studies have been concerning the examination of the adsorption onto walnut and hazelnut shells [6]. Cd(II) biosorption by walnut shell was studied by Bulut and Tez [7]. They reported 4.39, 4.65 and 4.90 mg/g for maximum sorption capacity at 25, 45 and 60 °C, respectively. The Langmuir sorption isotherm fitted the experimental data best with the regression coefficient $R^2 > 0.98$. Zn(II) biosorption by walnut shell was studied by Turan and Mesci [8] who reported 25.7 mg·g^{-1} for maximum sorption capacity at pH 8.

Temperature dependence of Cd(II) biosorption on hazelnut shell was studied by Bulut and Tez [9]. They reported 5.42, 5.45 and 5.47 mg·g^{-1} at 15, 45 and 65 °C, respectively, for maximum sorption capacity. Cimino et al. [6] reported 5.42 mg/g Zn(II) biosorption by hazelnut shell was studied by Cimino et al. [6] who reported 1.78 mg/g and Turan and Mesci [8] who reported 57.69 mg/g for maximum sorption capacity.

2. EXPERIMENTAL

The samples of orange peel originated from oranges (*Citrus sinensis*) imported from Argentina. The walnut and hazelnut shells were taken from local natural resources of

walnut (*Juglans regia L.*) and hazelnut (*Corylus avellana*) in Eastern Slovakia. The crude material was cleaned, rinsed with distilled water, and dried at 50 °C for 72 h. The dried samples were milled on a ball mill under 1.5 mm of particle size.

Zn(II) and Cd(II) solutions were prepared from analytic grade $ZnSO_4·7H_2O$ and $CdCl_2·2.5H_2O$, respectively, both obtained from ITES Vranov, Ltd. (SK). Analytic grade hydrochloric acid and sodium hydroxide were used to adjust pH, both obtained from ITES Vranov, Ltd. (SK).

The particle size distribution was estimated using a particle sizer Analysette 22 (Fritsch, D). The Sauter mean diameter of adsorbent particles, defined by the equation

$$d_{32} = \frac{\sum_{i=1}^{m} n_i d_i^{3}}{\sum_{i=1}^{m} n_i d_i^{2}}$$

where n_i is the mass percentage of the ith fraction (%), d_i is the mean particle size of the ith fraction (m), was used as a mean particle size for kinetic experiments.

The composition of the adsorbents was analysed using Elementary Vario Macro Cube (Elementar Analysensysteme GmbH, Germany).

Sorption experiments. The kinetic experiments were carried out at initial metal ion concentrations (C_0) of 10 and 100 mg/dm^3. Batch experiments were carried out in a continuously stirred glass vessel. The volume of the suspension, its temperature, the frequency of stirring, and the adsorbent dosage were 0.4 dm^3, 25 °C, 5 s^{-1}, and 1 g/dm^3, respectively. 1 cm^3 samples were taken at fixed time intervals directly from the solution. pH of the aqueous solution was 7.

For equilibrium experiments, flasks containing 0.2 dm^3 (V) of metal ion solution of various initial concentrations (1–1000 mg/dm^3) were used. The solutions were prepared from metal sulfate or chloride and a fixed dosage of sorbent (C_a = 1 g/dm^3). They were agitated for 2 h in a rotary shaker at 3.33 s^{-1}, with temperature control at 25 °C, what was sufficient for the metal ions adsorption to reach an equilibrium, based on the results of kinetics studies. The initial pH of the solution was 7.

The effects of pH (2, 5, and 7 at 25 °C) and temperature (30, 40, and 60 °C at pH 7) of initial solutions were tested prior to kinetics and equilibrium experiments for the initial metal ion concentration of 100 mg/dm^3. All the pH and temperature experiments were carried out in flasks containing 0.2 dm^3 of metal ion solution with a fixed dosage of sorbent 1 g/dm^3 and agitated for 2 h in a rotary shaker at 200 rpm.

After equilibration and sedimentation of suspensions, the samples were filtered through a micro filter of pore size 0.8 μm and the filtrates were analysed for metal content by AAS. The amounts of metal adsorbed q_e (mg/g) in each flask were determined

from the difference between the initial metal concentration C_0 and metal concentration at equilibrium C_e (mg/dm^3) in the solution according to the equation

$$q_e = \frac{(C_0 - C_e)V}{m_a}$$

where m_a (g) is the weight of adsorbent, V (dm^3) is the volume of solution.

The efficiency of heavy metal ions removal for the experiments on the effect of initial solution pH and the temperature was expressed

$$\text{Efficiency} = \frac{C_0 - C_e}{C_0} \times 100\%$$

Every experiment was performed three times and the result was taken as the average value of each experiment.

Data analysis. It is important to be able to predict the time needed to remove heavy metal the solution. Several models can be used to express the mechanism of solute sorption onto a sorbent. In the study, two different kinetic models were used to fit experimental data:
- pseudo-first order model

$$\frac{dq_t}{dt} = k_1 \left(q_e - q_t \right)$$

where q_t (mg/g) is the sorption capacity at time t (s), k_1 (1/min) is the rate constant of sorption [10]. After integrating and applying the boundary conditions for $t = 0$ and $t = t$, $q_t = 0$ and $q_t = q_t$, the equation is given as

$$\log \left(q_e - q_t \right) = \log \left(q_e \right) - \frac{k_1 t}{2.303}$$

- pseudo-second order approach

$$\frac{dq}{dt} = k_2 \left(q_{eq} - q_t \right)^2$$

k_2 (g/(mg·min) is the rate constant of the sorption [10]. From this equation for boundary conditions from $t = 0$ to $t = t$ and from $q_t = 0$ to $q_t = q_t$, after integration we arrive at

$$\frac{1}{q_{eq} - q_t} = \frac{1}{q_{eq}} + k_2 t \quad \text{or} \quad \frac{t}{q_t} = \frac{1}{k_2 q_{eq}^2} + \frac{t}{q_{eq}}$$

Kinetic studies not only give the equilibration time for the removal of heavy metals but also provide an insight into the mechanism of sorption. Generally, adsorption isotherms provide vital information on optimizing the use of adsorbents. Isotherm models offer an adequate description of metal adsorption equilibria on a wide range of adsorbent materials. The following isotherms were used:

• Freundlich isotherm represents the case when biosorption takes place on a heterogeneous surface with the interaction between the adsorbed molecules [11]

$$q_e = K_f C_e^{1/n}$$

where K_f $(dm^{3/n}/g^{1/n})$ is the adsorption capacity, n is the intensity of adsorption.

• Langmuir isotherm represents the case when biosorption takes place on a homogenous surface within the adsorbent [12]

$$q_e = \frac{q_m a_L C_e}{1 + a_L C_e}$$

q_m (mg/g) is the maximum sorption capacity, a_L (dm^3/mg) is a constant related to adsorption energy.

• Temkin isotherm assumes that a decrease in the heat of adsorption is linear and the adsorption is represented by a uniform distribution of binding energies [12]

$$q_e = \frac{RT \ln\left(K_{Te} C_e\right)}{a_{Te}}$$

K_{Te} (dm^3/g) is the equilibrium binding constant, a_{Te} (J/mol) is the heat of adsorption, R (8.314 J/(mol·K)) is a molar gas constant, T (K) is temperature.

• Dubinin–Radushkevich isotherm

$$q_e = q_m \exp\left(-\frac{\varepsilon^2}{2E^2}\right)$$

E (J/mol) is the energy of adsorption, ε (J/mol) is the Polanyi potential, which is used to describe the biosorption mechanism with a Gaussian energy distribution onto a heterogeneous surface [11].

• Redlich–Peterson isotherm

$$q_e = \frac{K_R C_e}{1 + a_R C_e^{\beta}}$$

K_R (dm^3/g) and a_R (dm$^{3\beta}$/mg$^{\beta}$) are constants, β is exponent which is used as a compromise between the Langmuir and Freundlich systems [11].

• Sips isotherm

$$q_e = \frac{q_m a_s C_e^{1/n}}{1 + a_S C_e^{1/n}}$$

a_s (dm$^{3/n}$/g$^{1/n}$) is the Sips constant related to the energy of adsorption which is a combination of the Langmuir and Freundlich isotherms and is likely to describe better heterogeneous surfaces [12].

• Toth isotherm

$$q_e = \frac{q_m C_e}{\left(K_{To} + C_e^{n_{To}} \right)^{1/n_{To}}}$$

K_{To} (g$^{n_{To}}$/dm$^{3n_{To}}$) is a constant, n_{To} is an exponent describing heterogeneous biosorption systems, it satisfies the limits of both low and high end boundaries of concentration [11].

• Khan isotherm is a generalized model for pure solutions [11]

$$q_e = \frac{q_m b_K C_e}{\left(1 + b_K C_e\right)^{a_K}}$$

b_K (dm^3/g) is a constant, a_K is an exponent.

Adsorption isotherms not only give the adsorption capacity but also provide information on the interaction of adsorbate with adsorbent, which can be important for the application of adsorbents.

Metal concentration analysis. The concentrations of unadsorbed metals were measured by the atomic absorption spectrometry (AAS, iCE 3300 Thermo Scientific, USA) with deuterium correction background [13]. The samples originating from kinetic and equilibrium experiments were centrifuged immediately after they were taken to settle any fine solid particles, and clear solutions were used for the analyses. If necessary, the samples were diluted with distilled water. The measurements were conducted at wavelengths of 213.9 and 228.8 nm with detection limits of 0.010 and 0.013 mg/dm^3 for Zn

and Cd, respectively. The standards for AAS were prepared from zinc standard solution of 1 mg/cm³ Zn in 2% HCl and cadmium standard solution, and 1 mg/cm³ Cd in 0.5 M HNO₃, both obtained from Acros Organics, Thermo Fisher Scientific Inc., Geel (BE) by dilution in distilled water.

Regression analysis. The adsorption kinetic models and the adsorption isotherms having two parameters can be transformed into linear forms to obtain adjustable parameters just by graphical means or by linear regression analysis. Nevertheless, for the models having more than two adjustable parameters, it is necessary to apply nonlinear least squares analysis. For those reasons, a minimization procedure has been adopted to solve isotherms and kinetic equations by minimizing the sum of error squared between the predicted values and the experimental data using the solver add-in function of the Microsoft Excel (Microsoft Corporation 2003). In order to quantitatively compare the applicability of isotherm equations in fitting to data, non-linear correlation coefficients (R^2) were calculated.

3. RESULTS AND DISCUSSION

3.1. PROPERTIES OF BIOSORBENTS AND KINETIC STUDIES

The particle size distributions of adsorbents are shown in Fig. 1, the Sauter mean particle diameter was 963, 1299, and 1117 µm and the mean particle diameter was 292, 1307, and 1029.5 µm, respectively. The chemical compositions of adsorbents (wt. %) were as follows:
- Orange peel: 49.2–52.5 of C, 5.24–5.4 of H, 0.7–0.8 of S, and 42.0–44.4 of O + N. The bulk density was 620 kg/m³.
- Walnut shell: 46.2–50.5 of C, 4.74–5.9 of H, 0.03 of S, and 42.1 of O + N. The bulk density was 630 kg/m³.
- Hazelnut shell: 42.67–51.90 of C, 4.80–5.95 of H, 0.02 of S, and 41.0–44.9 of O + N. The bulk density was 550 kg/m³.

The results of the experiments prior to kinetics studies showed that the optimum pH was 7. Concerning the temperature, the higher the temperature the higher the sorption capacity; for this reason, the ambient temperature of 25 °C was used.

The kinetics of Zn(II) adsorption on orange peel, walnut and hazelnut shells particles is shown in Fig. 2. Data in the figures show that adsorption is fast. The equilibrium for Zn(II) adsorption was achieved in approximately 120 min at 7.50, 4.78, and 3.65 mg/g onto orange peel, walnut and hazelnut shells, respectively, for the initial Zn(II) concentration of 100 mg/dm³. 90% of the equilibrium adsorption capacity was reached within the first 20 min for all the biosorbents. For the initial Zn(II) concentration of 10 mg/dm³, the equilibrium was achieved in approximately 60 min at 3.36, 2.35, and 2.39 mg/g onto

orange peel, walnut and hazelnut shells, respectively. 90% of the equilibrium adsorption capacity was also reached within the first 20 min for all the biosorbents.
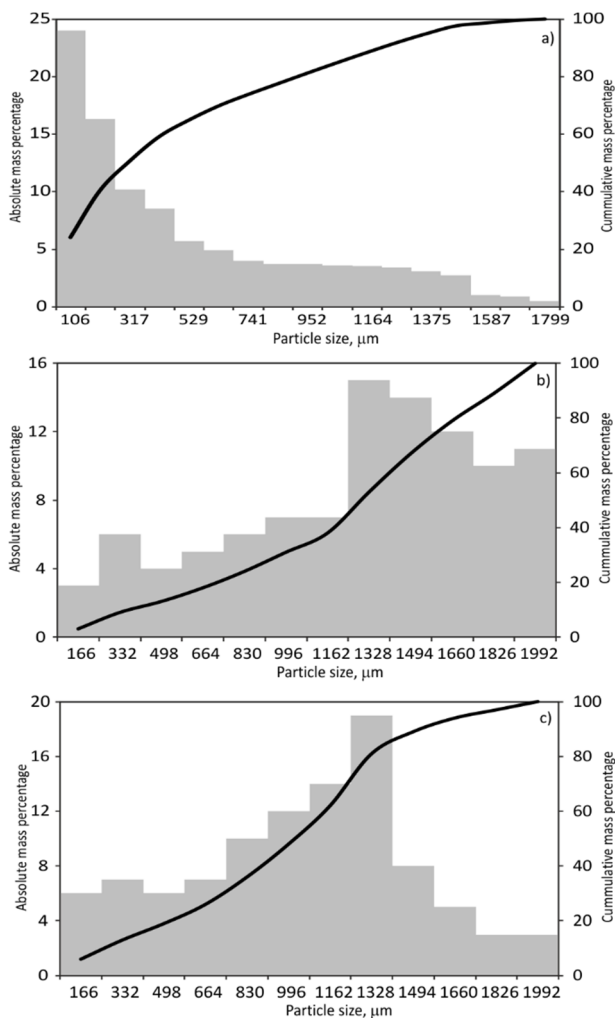

Fig. 1. Particle size distribution of:
a) orange peel, b) walnut shell, and c) hazelnut shell

The kinetics of Cd(II) adsorption on orange peel, walnut and hazelnut shells particles is shown in Fig. 3. Data in the figure show that the kinetics of adsorption is also fast. The equilibrium of Cd(II) adsorption was achieved in approximately 60 min at 7.50, 4.78, and 3.65 mg/g for the initial Cd(II) concentration of 100 mg/dm^3 and 4.50, 2.86, and 2.54 mg/g for the initial Cd(II) concentration of 10 mg/dm^3 onto orange peel, walnut and hazelnut shells, respectively. 90% of the equilibrium adsorption capacity

was reached within the first 20 min for the initial Cd(II) concentration of 100 mg/dm^3 and 10 min for the initial Cd(II) concentration of 10 mg/dm^3 for all the biosorbents.
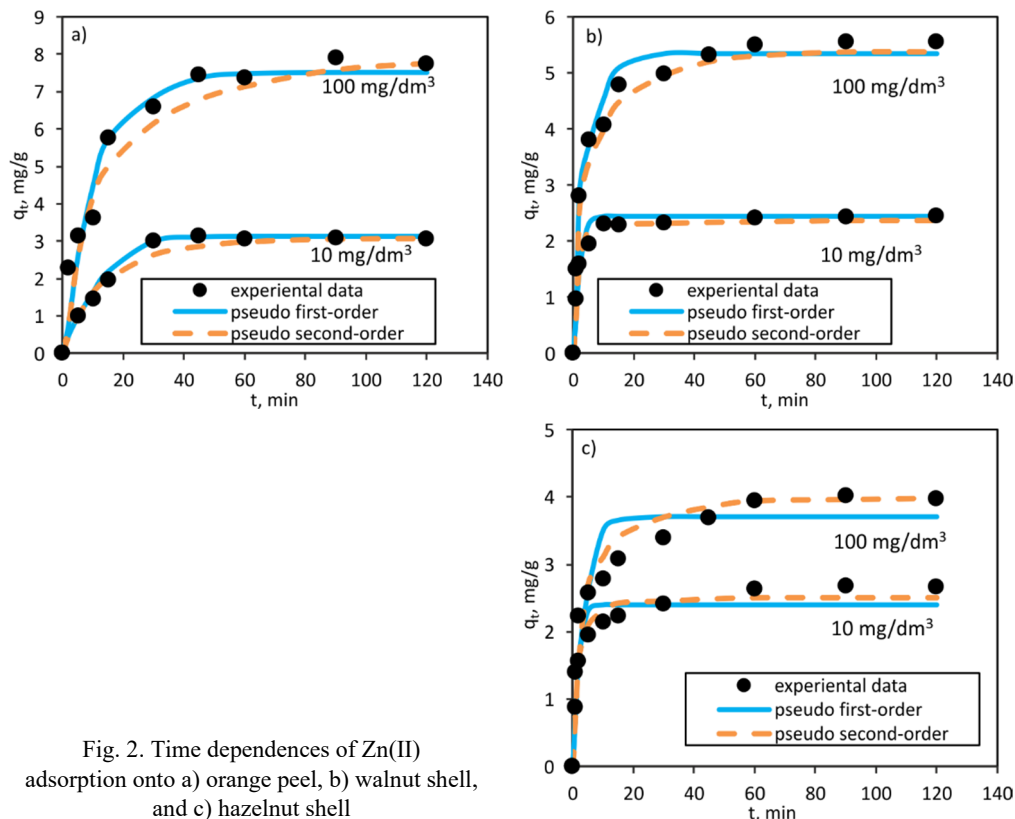

Fig. 2. Time dependences of Zn(II) adsorption onto a) orange peel, b) walnut shell, and c) hazelnut shell

Table 1

Kinetic parameters of adsorption of selected metals on orange peel, walnut shell, and hazelnut shell

| Order	Parameter	Orange peel				Walnut shell				Hazelnut shell			
		Zn(II)		Cd(II)		Zn(II)		Cd(II)		Zn(II)		Cd(II)	
		C_0 [mg/dm^3]											
		100	10	100	10	100	10	100	10	100	10	100	10
Pseudo-first	k_1, 1/min	0.081	0.084	0.094	0.636	0.200	0.516	0.209	1.565	0.297	0.801	0.520	0.396
	q_e, mg/g	7.500	3.364	10.981	5.004	5.310	2.388	10.886	2.821	3.650	2.345	10.458	3.178
	R^2	0.976	0.968	0.969	0.873	0.982	0.900	0.981	0.922	0.967	0.858	0.986	0.945
Pseudo-second	k_2, 1/min	0.009	0.034	0.008	0.15	0.042	0.520	0.020	0.838	0.089	0.373	0.062	0.121
	q_e, mg/g	8.636	3.376	12.4	5.453	5.54	2.292	12.087	2.292	3.984	2.535	11.296	3.619
	R^2	0.962	0.972	0.959	0.955	0.972	0.965	0.965	0.966	0.901	0.949	0.932	0.977
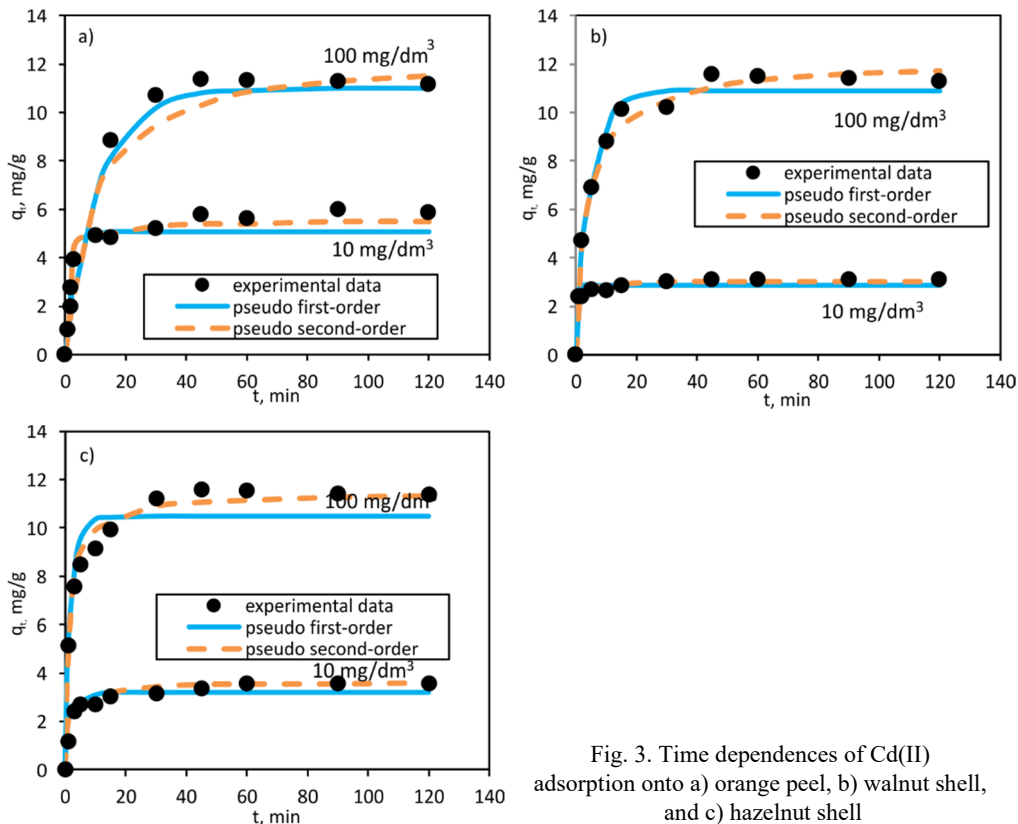
Fig. 3. Time dependences of Cd(II) adsorption onto a) orange peel, b) walnut shell, and c) hazelnut shell

The sorption kinetics was studied using two kinetics models – pseudo-first order and pseudo-second order and the calculated rate constants k_1, and k_2 and correlation coefficients for Zn and Cd onto orange peel are shown in Table 1.

3.2. EQUILIBRIUM STUDIES

Based on the results of the kinetic experiments, the contact time for adsorption was set to 2 h in the equilibrium sorption experiments. The parameters of the isotherms for Zn(II) and Cd(II) adsorption onto orange peel, walnut and hazel nut shell are given in Table 2.

The maximum sorption capacity of Zn(II) and Cd(II) onto orange peel was 15.51 and 19.8 mg/g, respectively. The equilibrium data and the fitted data of Zn(II) and Cd(II) adsorption by two-parameter and three-parameter isotherms are shown in Fig. 4. The correlation coefficients are from 0.737 to 0.930 and from 0.669 to 0.968 for Zn(II) and Cd(II), respectively. Based on the regression analysis and the fit in the figures, the best describing correlations are the Khan isotherm for Zn(II) adsorption and that of Redlich –Peterson for Cd(II) adsorption.

Adsorption isotherm parameters of selected metals on orange peel, walnut shell, and hazelnut shell

Isotherm	Parameter	Orange peel		Walnut shell		Hazelnut shell	
		Zn(II)	Cd(II)	Zn(II)	Cd(II)	Zn(II)	Cd(II)
Freundlich	K_f, dm$^{3/n}$/g$^{1/n}$	2.89	1.37	0.67	1.78	0.11	3.26
	n	4.01	2.39	2.39	2.97	1.18	3.40
	R^2	0.9294	0.9675	0.9369	0.9014	0.9580	0.9456
Langmuir	q_m, mg/g	15.51	19.80	11.55	16.66	26.61	21.10
	a_L, dm^3/mg	0.01	0.01	0.01	0.01	0.01	0.01
	R^2	0.8890	0.9569	0.8837	0.9188	0.9604	0.9605
Temkin	K_{Te}, dm^3/g	0.23	0.06	0.20	0.10	–	0.12
	a_{Te}, J/mol	854	475	1346	712	–	526
	R^2	0.9294	0.9614	0.8979	0.9209	–	0.9636
Dubinin–Radushkevich	q_m, mg/g	23.04	28.48	23.17	24.01	14.85	27.34
	E, J/mol	14.21	16.19	8.58	16.49	15.47	18.86
	R^2	0.7371	0.6690	0.5570	0.7600	0.7126	0.7665
Redlich–Peterson	K_R, dm^3/g	14.59	1.28	5.16	2.08	0.16	2.14
	a_R, dm$^{3\beta}$/mg$^\beta$	7.49	0.72	7.38	1.02	0.82	0.72
	β	0.68	0.61	0.59	0.68	0.23	0.69
	R^2	0.9282	0.9688	0.9366	0.9046	0.9594	0.9465
Sips	q_m, mg/g	16.08	26.15	13.10	24.87	84.80	36.21
	a_s, dm$^{3/n}$/g$^{1/n}$	0.02	0.01	0.01	0.02	0.01	0.03
	B	1.06	1.17	1.12	1.54	1.03	1.69
	R^2	0.8947	0.9649	0.8855	0.9196	0.9665	0.9625
Toth	q_m, mg/g	23.98	28.23	13.99	28.20	31.90	28.11
	K_{To}, g$^{n_{To}}$/dm$^{3n_{To}}$	99.44	172.71	70.66	159.89	395.48	137.71
	n_{To}	0.95	0.98	0.94	0.95	0.96	0.93
	R^2	0.8695	0.9573	0.7163	0.9150	0.9554	0.9655
Khan	q_m, mg/g	2.75	0.20	0.62	2.70	0.78	3.71
	b_K, dm^3/g	1.31	7.54	0.38	0.38	0.16	0.36
	a_K	0.75	0.45	0.49	0.68	0.28	0.68
	R^2	0.9304	0.9663	0.9409	0.9045	0.9646	0.9437

In the adsorption process, the maximum adsorption capacity for removal of Zn(II) and Cd(II) using walnut shell was 11.55 and 16.65 mg/g, respectively. The equilibrium data and the fitted data of Zn(II) and Cd(II) adsorption by two-parameter and three- -parameter isotherms are shown in Fig. 5. The correlation coefficients are in the range of 0.557–0.940 and 0.760–0.920 for Zn(II) and Cd(II), respectively. Based on the re- gression analysis and the fit in the figures, the isotherms best describing adsorption are the Khan isotherm for Zn(II) and that of Temkin for Cd(II) adsorption.

In the adsorption process, the maximum adsorption capacity for removal of Zn(II) and Cd(II) using hazelnut shell was 26.60 and 21.10 mg/g, respectively. The equilibrium

data and the fitted data for Zn(II) and Cd(II) adsorption are shown in Fig. 6. The correlation coefficients are in the range of 0.712–0.966 and 0.766–0.965 for Zn(II) and Cd(II), respectively. The isotherms best describing adsorption are the Sips isotherm for Zn(II) and that of Toth for Cd(II).
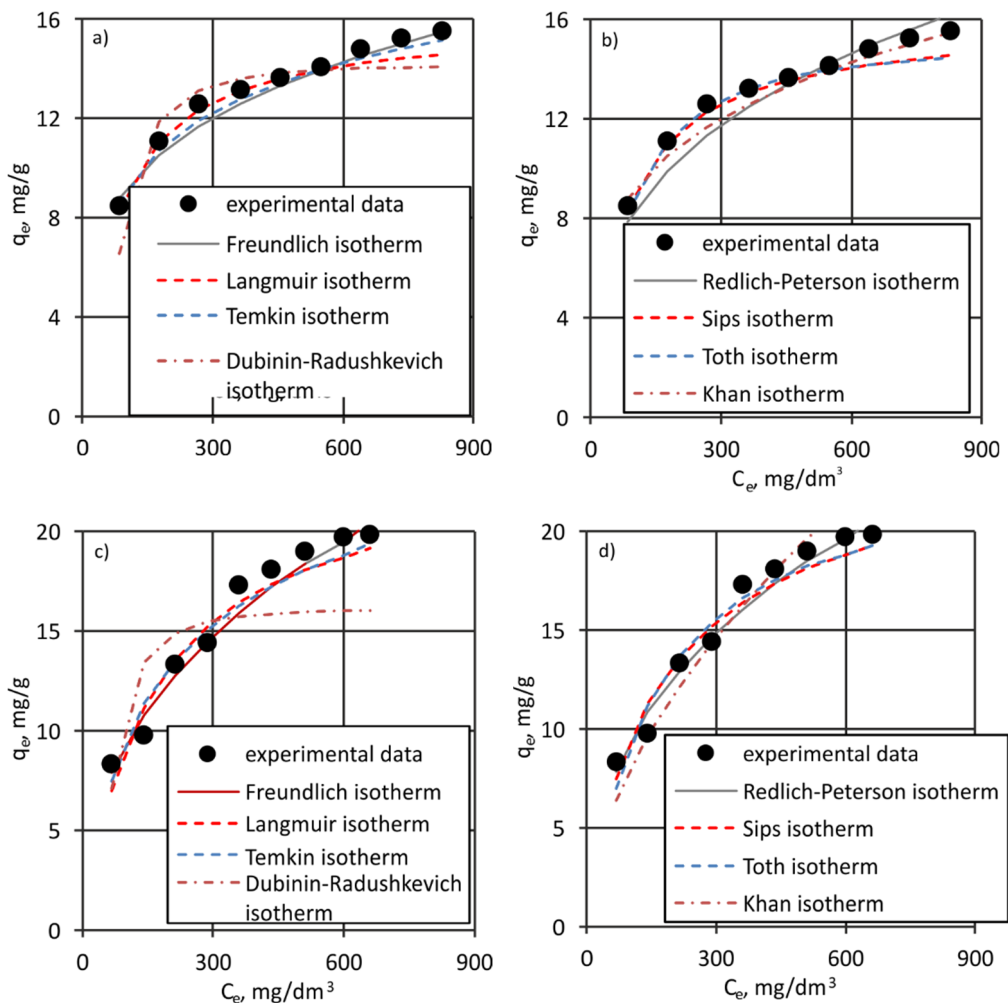

Fig. 4. Adsorption on orange peel of Zn(II) described by a) two-parameter, b) three-parameter isotherms, and of Cd(II) described by c) two-parameter, and d) three-parameter isotherms

The effect of pH on zinc and cadmium adsorption was examined for acid (pH 2), weak acid (pH 5), and neutral (pH 7) solution. The effect of pH on the removal of Zn(II) and Cd(II) is shown in Fig. 7. Upon increasing pH, the amount of Zn(II) and Cd(II) removed is also increasing.
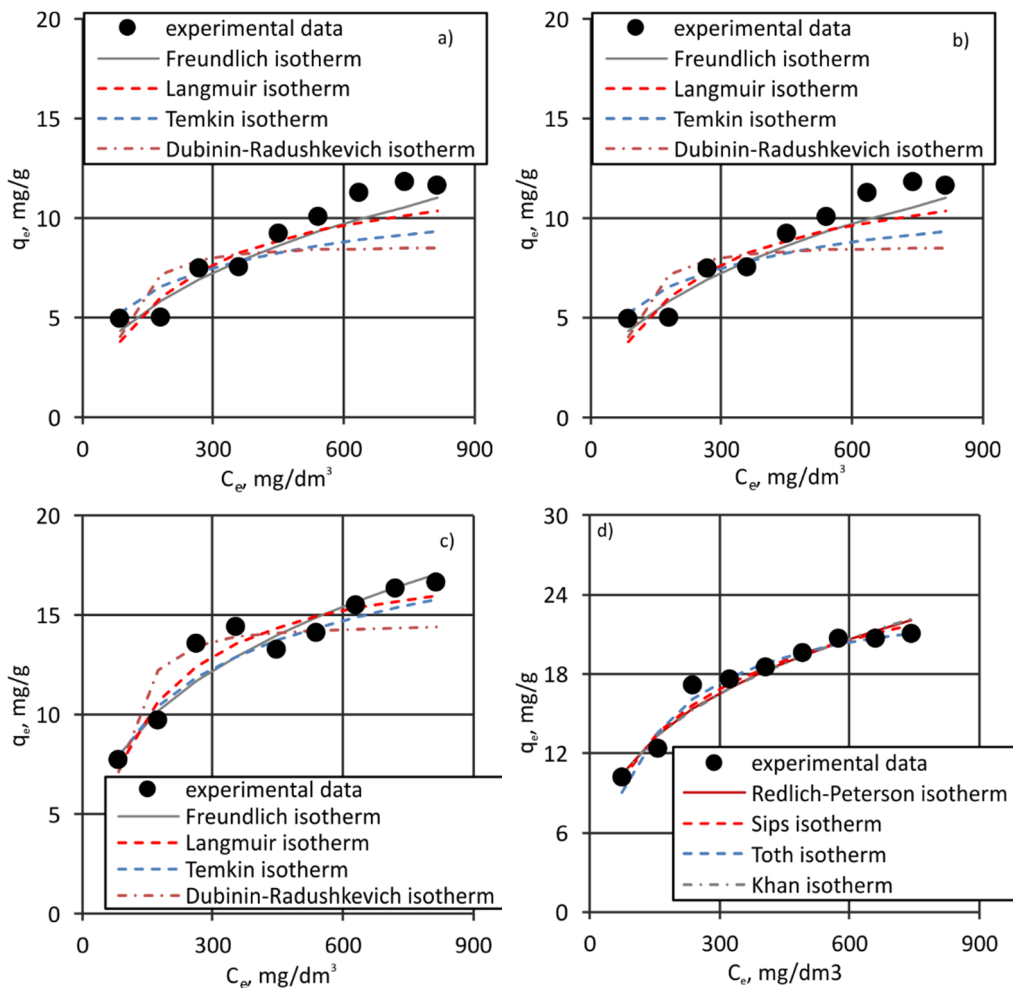
Fig. 5. Adsorption on walnut shell of Zn(II) described by a) two-parameter, b) three-parameter isotherms and of Cd(II) described by c) two-parameter, and d) three-parameter isotherms

The effect of temperature on the removal of Zn(II) and Cd(II) is shown in Fig. 8. For all the studied biosorbents it was found that the efficiency of Zn(II) and Cd(II) removal increased upon increasing temperature.

There are several factors affecting the biosorption of Zn(II) and Cd(II) and other heavy metals. Biosorption includes processes such as adsorption, ion exchange, precipitation, complexation, chemisorption, condensation, etc. [14, 15]. Plant cells consist of cellulose molecules in the form of microfibers surrounded by hemicellulose, lignin, pectin, and proteins, and also contain functional groups that facilitate the binding of heavy metal ions [5, 16]. The binding ability of cellulose molecules depends on crystallinity,

specific surface area, and degree of polymerization [17, 18]. Other factors affecting the binding ability, i.e., sorption capacity are as follows [5, 16–19]:

• initial concentration of metal in solution which affects the amount of adsorbed metal as far as the maximum sorption capacity is reached,

• initial pH of solution but it also affects the form of metals in solution as at higher concentrations (above 8–9) most heavy metals occur in the form of hydroxide precipitates,

• contact time which is in most cases as short that about 90% of the capacity of biosorbent is filled in a few minutes.
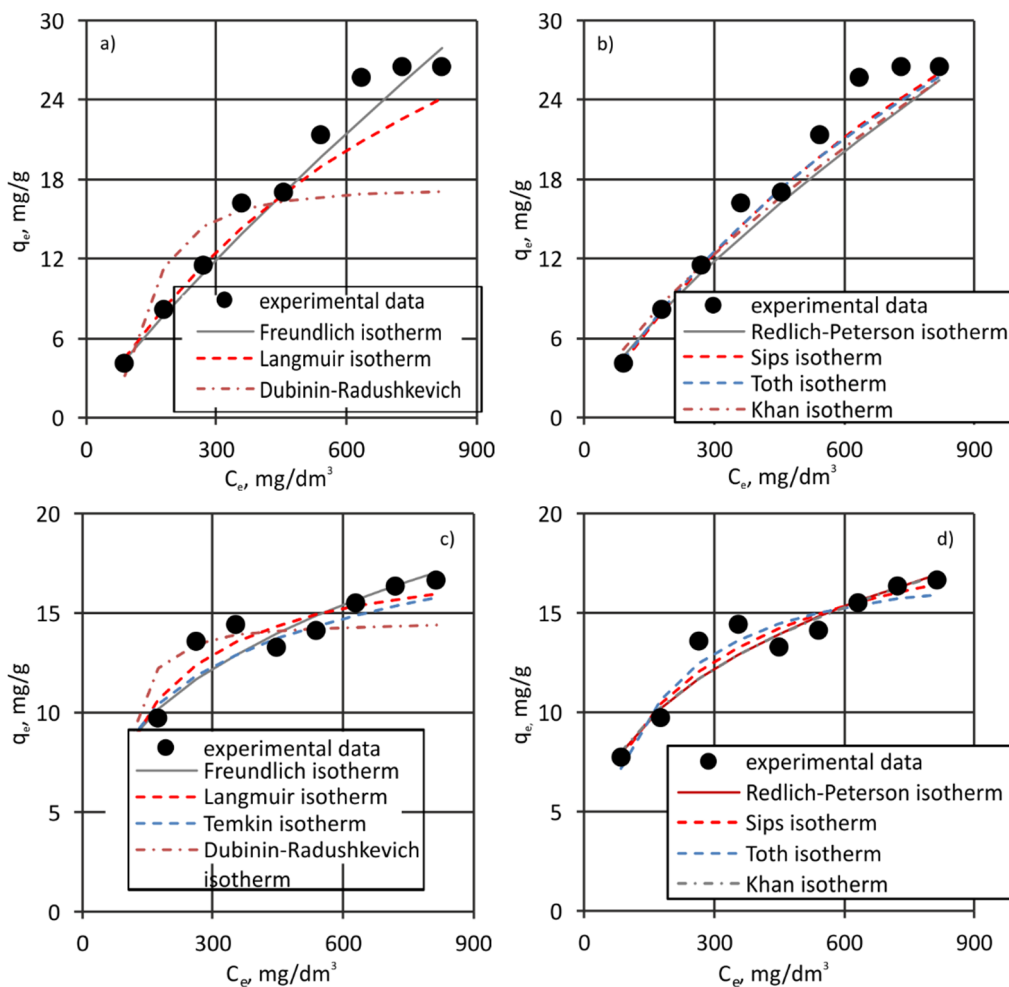

Fig. 6. Adsorption on hazelnut shell of Zn(II) described by a) two-parameter, b) three-parameter isotherms and of Cd(II) described by c) two-parameter, and d) three-parameter isotherms
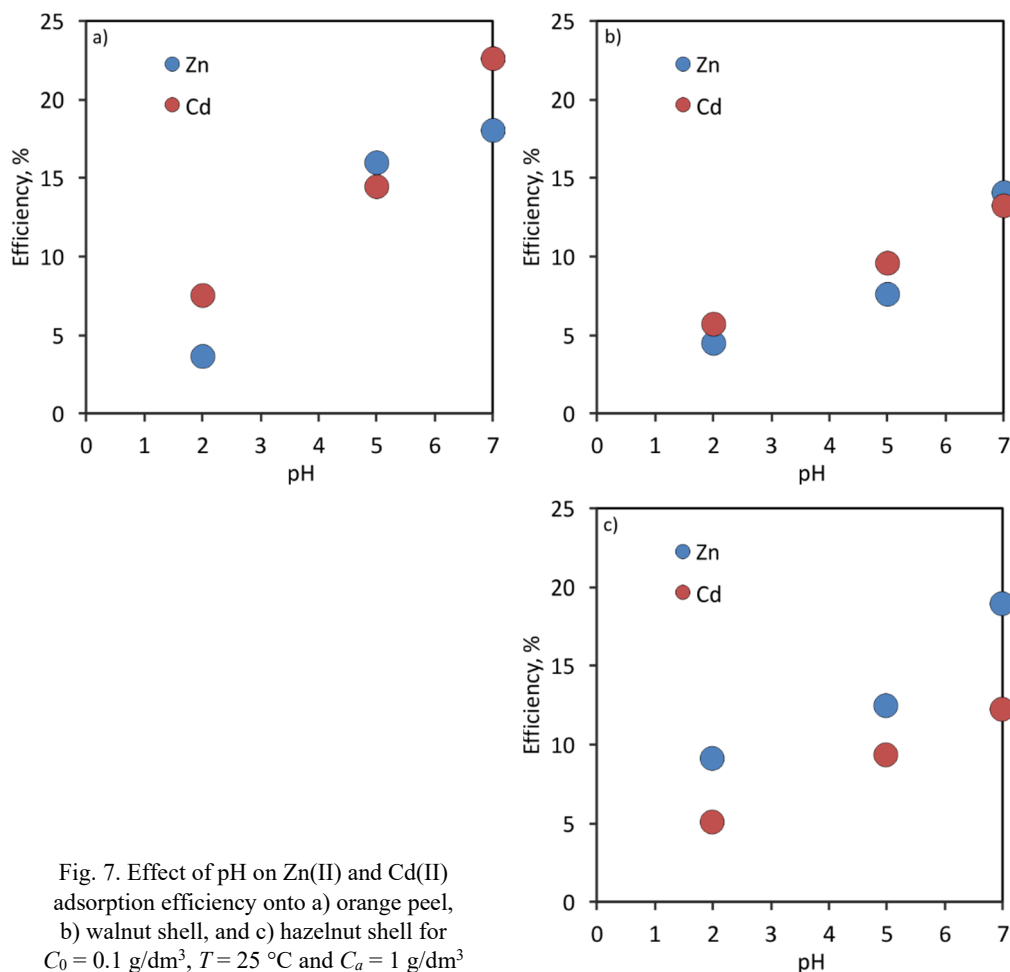
Fig. 7. Effect of pH on Zn(II) and Cd(II) adsorption efficiency onto a) orange peel, b) walnut shell, and c) hazelnut shell for $C_0 = 0.1$ g/dm^3, $T = 25$ °C and $C_a = 1$ g/dm^3

For the above reasons we studied the kinetics and the equilibrium sorption capacity of ions on biosorbents in function of equilibrium concentration of ions in the solution and time, respectively. The biosorption process of both Zn(II) and Cd(II) on all the studied biosorbents occurs in two phases. The first one is probably fast sorption of ions onto the outer surface documented by the time of reaching 90% of the capacity within 10–30 min. The second phase is slower (30–90 min), possibly caused by inner-particle diffusion below the surface of the biosorbents [20, 21]. A different reason for the two-stage sorption process is probably that sorption develops in two different types of binding sites. Chemisorption and inner-sphere complexation are usually fast; on the contrary ion exchange and physical sorption on solid surface are usually slow [20, 22]. The fast sorption process and high equilibrium sorption capacity can suggest that chemisorption or inner-sphere complexation are processes controlling the sorption of metal ions onto the biosorbents [20, 23].
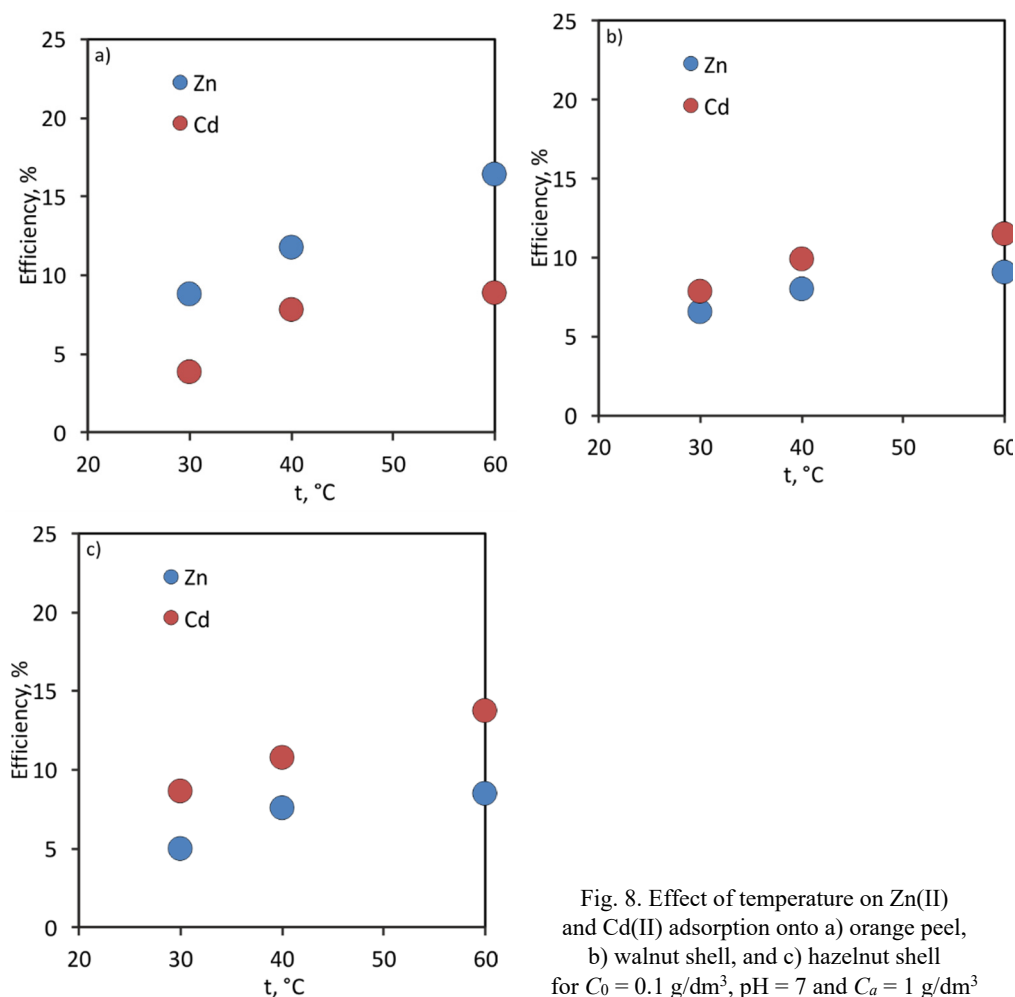
Fig. 8. Effect of temperature on Zn(II)
and Cd(II) adsorption onto a) orange peel,
b) walnut shell, and c) hazelnut shell
for $C_0 = 0.1$ g/dm^3, pH = 7 and $C_a = 1$ g/dm^3

For kinetic experiments with $C_0 = 100$ mg/dm^3, the pseudo-first order model provides better correlation for both zinc and cadmium sorption than the pseudo-second order thus the pseudo-first order model better describes the sorption kinetics. This fact indicates that biosorption is either controlled by the transport of molecules from the solution to the adsorbent or independent on the rate [24]. For kinetics experiments with $C_0 = 10$ mg/dm^3, the pseudo-second order model provides better correlation for both zinc and cadmium sorption than the pseudo-first order thus the pseudo-second order model better describes the sorption kinetics process. This fact indicates that the sorption rate of both Zn(II) and Cd(II) at lower concentration depends only on ion concentrations at the surface of the biosorbent and the sorption kinetics is probably primarily controlled by chemical sorption [24]. The results are in accordance with the theoretical results [24] implying that the surface coverage fraction, i.e., the coverage of biosorbent surface by

the reaction products is higher at lower ion concentrations thus obeying the pseudo--second order model and vice versa the surface coverage fraction is lower at higher ion concentrations thus obeying the pseudo-first order model.

The maximum sorption capacity of Zn(II) and Cd(II) onto the orange peel was 15.51 and 19.8 mg/g, respectively. The amount of Cd(II) ions removed onto orange peel is higher compared to that of Zn(II) ions, which confirms the results of the study by Liang et al. [25]. Li et al. [2] reported the maximum sorption capacity of 49.70 and 55.08 mg/g, respectively. The difference is caused by different particle size; in our study we used particles of size between 0.1 and 1.8 mm, while in the study by Li et al. [2] it was size between 0.1 and 0.2 mm. Pérez-Marín et al. [3] reported the maximum sorption capacity of 44.96, 46.09 and 48.34 mg/g for pH 4, 5 and 6, respectively, for Cd(II). Though the pH values are lower than 7, the adsorption capacities are higher than the presented results. This may also be connected with the particle size smaller than 1.5 mm. Orange peel is also effective for removal of other toxic metals, e.g., Cu(II) – 44.28 mg/g [1], Co(II) – 37.13 mg/g [2], Ni(II) – 27.00 mg/g [2].

Turan and Mesci [8] reported 25.7 mg/g for maximum sorption capacity of Zn(II), the measurement was done at pH 8, therefore the precipitation of zinc in the form of $Zn(OH)_2$ occurred depending on the concentration of Zn(II) (the higher the concentration the higher the precipitation) and temperature (at higher temperature precipitation occurs at lower concentration of Zn(II) and pH).

Walnut shell is also effective on removal of other toxic metals, e.g., Cu(II) – 21.28 mg/g, Pb(II) – 6.54, 6.68 and 6.66 mg/g at 25, 45 and 60 °C, respectively [1], Cu(II) – 21.28 mg/g at pH 6 [8], Ni(II) – 2.40, 2.68 and 2.79 mg/g at 25, 45 and 60 °C, respectively [1].

The maximum adsorption capacity for removal of Zn(II) and Cd(II) onto hazelnut shell was 26.60 and 21.10 mg/g, respectively. Bulut and Tez [9] reported the maximum sorption capacity of 5.42, 5.45 and 5.47 mg/g at 15, 45 and 65 °C, respectively, for Cd(II) and Cimino et al. [6] reported 5.42 mg/g at pH 4. The maximum sorption capacity is lower than the capacity reported in our study which is caused by different particle size – 0.8 mm [7], though it does not fit the general theory as in our study the particle size was 0.2–2.0 mm, with mean particle size of 1.0 mm, thus the cause for different sorption capacities might also be the initial pH value.

Cimino et al. [6] reported 1.78 mg/g at pH 4 for maximum sorption capacity of Zn(II). In their study, pH 4.0 was found to be the optimum value for sorption. On the other hand Turan and Mesci [8] reported 57.69 mg/g for maximum sorption capacity at pH 8 but this high capacity is not only the result of adsorption but also precipitation as explained above. Hazelnut shell is also effective for removal of other toxic metals, e.g., Cr(III) – 3.08 mg/g [6], Cu(II) – 35.61 mg/g [8].

Dubinin–Radushkevich isotherm can also be used to estimate the adsorption mechanism based on the potential theory assuming heterogeneous surface [11, 12, 26]. The free energy of biosorption is the energy of transport of 1 mol of a heavy metal ions from

the solution to the surface of biosorbent. The value of adsorption energy can also be used for estimation of the type of adsorption mechanism [11, 12]. If the adsorption energy is in the range of 8–16 kJ/mol, the type of adsorption is ion exchange [12]. If it is in the range of 1–8 kJ/mol, adsorption is physical and if it is above 16 kJ/mol, chemisorption occurs [26]. For the biosorbents examined in the present study, the Zn(II) adsorption mechanism is probably ion exchange and the Cd(II) adsorption mechanism is probably chemisorption.

The relationship between adsorption and temperature is directly proportional. The higher the temperature, the more effective biosorption but also more energy is required. The minimum biosorption efficiency is achieved in acidic environment (pH 2) which can be caused by high concentration and high mobility of H^+ ions. In this case, hydrogen ions are preferentially adsorbed to zinc and cadmium ions. At pH 7, the concentration of hydrogen ions is lower, and therefore Zn(II) and Cd(II) ions are preferably adsorbed [1].

Based on the results of sorption equilibrium experiments, Zn(II) adsorption onto orange peel, walnut and hazelnut shell probably occurs on a heterogeneous surface with interaction between the adsorbed molecules for pure solutions. Cd(II) adsorption onto these adsorbents probably also occurs on a heterogeneous surface.

4. CONCLUSION

The studied biosorbents were suitable for the removal of Zn(II) and Cd(II) ions. The highest removal efficiency of Zn(II) and Cd(II) ions was obtained for hazelnut shells. Orange peel and walnut shell also demonstrated high sorption ability of Cd(II) ions. According to the efficiency of sorbents, they can be arranged in a following way: Zn(II) – hazelnut shell > walnut shell > orange peel, and Cd(II) – hazelnut shell > orange peel > walnut shell. The biosorption process was fast. About 90% of Zn(II) and Cd(II) ions were removed within 20 min. The adsorption is also influenced by pH and temperature. The optimum pH was 7. The sorption capacity was directly proportional to temperature which implies that the sorption process was probably chemisorption. This fact was also suggested by the result of kinetics studies while the equilibrium studies suggest that the sorption possibly occurs on a heterogeneous surface.

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