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Sorption of 4-chlorophenol and lead(II) on granular activated carbon: equilibrium, kinetics and thermodynamics

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ABSTRACT

In the presented study, the kinetics, equlibrium and thermodynamics of simultaneous sorption of 4-chlorophenol (4-CP) and lead(II) (Pb(II)) from aqueous solutions are investigated and described. The granular activated carbon Norit ROW 0.8 Supra was used as sorbent. The sorption process was carried out at various temperatures (283, 293 K). The kinetic models, such as pseudo-first-order and pseudo-second-order, and the Weber-Morris intraparticle diffusion model, were used to describe the sorption rate and mechanism. Both the sorption of the Pb(II) and the 4-CP at 283 and 293 K temperatures followed the pseudo-second-order kinetic model. The equilibrium data were analyzed by the Langmuir, Freundlich, Redlich–Peterson and Langmuir–Freundlich models by using the non-linear regression technique. The sorption equilibrium of both of the sorbates at 283 K on the Norit carbon was best described by the Langmuir–Freundlich isotherm equation. At a temperature of 293 K the sorption of the Pb(II) was best described by the Redlich–Peterson isotherm equation ($R^2 = 0.9951$), but in the case of the 4-CP, the sorption was best described by both the Redlich–Peterson and the Freundlich models. The equilibrium of the 4-CP sorption on the granular activated carbon was established faster than the Pb(II) sorption. The presence of the 4-CP slowed down the Pb(II) sorption. The sorption of the 4-CP and the Pb(II) on the granulated activated carbon has a positive character and is favourable. Gibb's free energy showed that the Pb(II) and 4-CP sorption are spontaneous processes. Proposed in this paper is the manner of carrying out the research and the processing of the research results which can be applied to other multicomponent water pollution systems.

Keywords: GAC; Lead; Phenols; Sorption

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1. Introduction

Industrial effluents containing organic and inorganic environmental pollutants pose a serious problem because of their toxicity, resistance to degradation and ability to accumulate. Among them, chlorophenols and heavy metals are particularly dangerous due to their widespread presence in aquatic environments and the fact that they are poisonous to aquatic life [1–4]. In the present study, 4-chlorophenol (4-CP) and lead(II) (Pb(II)) were chosen as representatives of chloroorganic contaminants and heavy metals, respectively.

The removal of toxic substances such as organic pollutants and heavy metals from water is currently one of the most important environmental problems. Various conventional methods have been designed and used to remove 4-CP and Pb(II) from water. Among all of the possible techniques, sorption, especially on the activated carbons, was

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found to be the most effective method for the removal of chlorophenols and heavy metals from water due to their well-developed internal pore structure and surface area, high sorption capacity and simplicity of operation. The sorption of 4-CP on activated carbons has been described by: Jung et al. [5], Hamdaoui and Naffrechoux [6,7], Hameed et al. [8], Deryło-Marczewska et al. [9,10], Tseng et al. [11], Lorenc-Grabowska et al. [12], Biniak et al. [13] and Kuśmierek et al. [14,15]. The sorptive removal of Pb ions is also well documented by: Shekinah et al. [16], Payne and Abdel-Fattah [17], Goel et al. [18], Gueu et al. [19], Gercel and Gercel [20], Prado Cechinel et al. [21]. Most of the papers refers to the sorption of organic contaminants or heavy metals only, although both of these groups, including 4-CP and Pb(II), may be present in the aquatic environment simultaneously. Only a few works describe the simultaneous sorption of heavy metals and organic pollutants. Pei et al. [22] studied the effect of lead on the sorption of 2,4,6-trichlorophenol on soil and peat. Andini et al. [23] described simultaneous sorption of 2-chlorophenol and Pb and Cd ions on organophilic bentonite while Quintelas et al. [24] investigated the competitive sorption of ortho-cresol, phenol, chlorophenol and Cr ions by a bacterial biofilm on granular activated carbon. The simultaneous sorption of lead(II) and phenol onto the montmorillonites [25], dried anaerobic sludge [26] as well as onto the modified and unmodified activated carbons [26–31] was also reported. However, to the best of our knowledge, the competitive sorption of Pb(II) and 4-CP in the solutions using activated carbon has not been studied.

The aim of this work was to examine simultaneous sorption of Pb(II) and 4-CP on the granular activated carbon Norit ROW 0.8 Supra. This kind of carbon is commonly used for water purification.

2. Materials and methods

2.1. Preparation of the carbon sorbent, Pb(II) and 4-CP solution

The sorption studies were conducted using commercial granular activated carbon Norit ROW 0.8 Supra, extruded and cylindrical shaped with a grain of diameter 0.8 mm. Its porous structure was characterized on the basis of the nitrogen low temperature (77 K) adsorption-desorption isotherm (ASAP 2020, Micromeritics). The main parameter values were as follows: the specific surface area S_{BET} = 970 m^2·g^{-1}, the micropore volume V_{mi} = 0.325 cm^3·g^{-1}, the mesopore volume V_{me}= 0.250 cm^3·g^{-1}, the specific surface of mesopores S_{me} = 145 m^2·g^{-1} The surface oxygen functional group contents were obtained from the NaOH and HCl (0.1 mol·L^{-1}) neutralization and were equal to 0.45 mmol·g^{-1} for the acidic ones and 0.39 mmol·g^{-1} for the basic, respectively. The material was washed with tap water, and then redistilled water. Finally, the washed activated carbon was dried at room temperature. The weighed portions were prepared on an analytical balance to the nearest 0.0001 g.

The lead was introduced into the solution in the form of lead(II) nitrate $Pb(NO_3)_2$ Chempur (Poland) and the 4-chlorophenol was purchased from Sigma (St Louis, MO, USA).

The concentration of the Pb(II) was determined at a wavelength of 205.3 and 217.0 nm by using an atomic absorption spectrophotometer PGI990 (PG Instruments Ltd, Great Britain). The initial and final concentrations of the 4-CP in the water solutions were measured by HPLC with a diode array detector (Shimadzu LC-20, Kyoto, Japan). The analyte was separated on a Phenomenex Luna C18 (4.6 × 150 mm, 3 μm) column (Torrance, CA, USA). The chromatographic measurements were carried out under isocratic conditions operated at 313 K with acetonitrile and water adjusted to pH 3.0 with acetic acid (80:20, v/v). The mobile phase was pumped at a flow rate of 0.6 ml/min, and peaks were monitored at 281 nm.

2.2. Sorption kinetics

Investigations of the sorption kinetics were carried out under static conditions. Erlenmeyer flasks with a certain weight of sorbent (0.5 g), solutions (100 mL) lead nitrate $Pb(NO_3)_2$ and 4-CP were shaken with the use of thermostated shakers at temperatures of 283 and 293 K. The sorbent contact time with the sorbate solution was variable. The sorption kinetics investigation was carried out until the sorption reached equilibrium. A maximum time of shaking of 300 min was adopted. The sorption capacity in time q_t, (mmol·g^{-1}) was calculated with the use of Eq. (1):

$$q_t = \frac{(C_0 - C_t)\cdot V}{m} \tag{1}$$

where C_0, C_t– the initial and the current concentrations of the Pb(II)/4-CP, mmol·L^{-1}; m – the activated carbon mass, g; V – the volume of the solution, L.

2.3. Sorption equilibrium studies

The sorption experiments were carried out by shaking out the Norit carbon samples of various mass (0.1–1.0 g) with 50 ml of aqueous solution of Pb(II) and 4-CP of the desired concentrations 0.1 and 0.5 mmol·L^{-1} for each. Sorption isotherms were made at 283 and 293 K. The time of the equilibration was 3 h. The amount of the Pb(II) and 4-CP sorption at the equilibrium q_e (mmol·g^{-1}), was calculated using the Eq. (2):

$$q_e = \frac{(C_0 - C_e)\cdot V}{m} \tag{2}$$

where C_0 – the initial sorbate concentration, mmol·L^{-1}; C_e – the equilibrium concentration of sorbate, mmol·L^{-1}; m – the mass of the activated carbon used, g; V – the volume of the solution, L.

2.4. Modelling

2.4.1. Kinetic models based on the order of reaction

Lagergren's kinetic pseudo-first-order (Eq. 3) [32] and pseudo-second-order (Eq. 4) [33] models were analysed:

$$q_t = q_e(1 - e^{-k_1 t}) \tag{3}$$

$$q_t = \frac{k_2 \cdot q_e^2 \cdot t}{1 + k_2 \cdot q_e \cdot t} \tag{4}$$

where q_e – the amount of sorption at the equilibrium, q_t – the amount of sorption at the time t, k_1 – the rate constant of the pseudo-first-order sorption process, k_2 – the rate constant of the pseudo-second-order sorption process, t – time.

2.4.2. Diffusive kinetic model

The Weber-Morris model [34] was analysed (Eq. 5):

$$q_t = k_{id} \cdot t^{0.5} + c \tag{5}$$

where k_{id} – Weber-Morris kinetic constant, c – intercept from Weber-Morris equation.

2.4.3. Equilibrium models

The Langmuir [35], Freundlich [36], Redlich–Peterson [37] and Langmuir–Freundlich [7] isotherms were used. They are given, respectively, by Eqs. (6)–(9):

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

$$q_e = K_F \cdot C_e^{\frac{1}{n}} \tag{7}$$

$$q_e = \frac{A \cdot C_e}{1 + B \cdot C_e^g} \tag{8}$$

$$q_e = \frac{q_{mLF} \cdot (K_{LF} \cdot C_e)^{m_{LF}}}{1 + (K_{LF} \cdot C_e)^{m_{LF}}} \tag{9}$$

In the Langmuir model, q_m is the maximum adsorption capacity, b is the constant related to the free energy of adsorption. In the Freundlich model, K_F is a constant indicative of the relative adsorption capacity of the adsorbent, n is a constant indicative of the intensity of the adsorption. A is the Redlich–Petrson constant, B is also a constant and g is an exponent that lies between 0 and 1. At the high liquid-phase concentrations of the adsorbate Eq. (8) reduces to the Freundlich equation where A/B and $(1 - g)$, respectively, the parameters K_F and $1/n$ of the Freundlich model. For $g = 1$, Eq. (8) reduces to the Langmuir equation, with $b = B$ is the Langmuir adsorption constant related to the energy of adsorption and $A = bq_{mL}$, where q_{mL} signifies the Langmuir adsorption capacity of the adsorbent. In the Langmuir–Freundlich model q_{mLF} is the Langmuir–Freundlich maximum adsorption capacity, K_{LF} equilibrium constant for a heterogeneous solid, and m_{LF} is the heterogeneity parameter, lies between 0 and 1.

All of the model parameters were evaluated by nonlinear regression using the *solver* add-in with Microsoft Excel. In this study, commonly used error functions, i.e., the determination coefficient (R^2) and Chi-square (χ^2) function were examined for each set of experimental data.

2.5. Thermodynamics

The thermodynamic parameters of ΔGº for the sorption processes are calculated using the following equation (10) [38,39]:

$$\Delta G^\circ = -RT \ln b \tag{10}$$

where R is universal gas constant (8.314 J·mol^{-1}·K^{-1}), b is the constant related to the free energy of sorption (L·mmol^{-1}) and T is the absolute temperature in K.

3. Results and discussion

3.1. Sorption kinetic

The equilibrium of the sorption process is achieved when the chemical potential of the sorbate in the solution is equal to the chemical potential of the sorbate in adsorbed state. With the increase of the shaking time, the amount of the Pb(II) and 4-CP removed from the solution increased, however, only up to the point that they reached the sorption equilibrium. In both the case of the Pb(II) as well as the 4-CP, at first stage the process is fast, then more slowly and less efficiently. As shown in Fig. 1, the equilibrium of the 4-CP sorption on granular activated carbon is established in a rather short period of time. After 60 min a high degree of reduction of the 4-CP was obtained - above 90% (95% at 283 K and 93% at 293 K). For the Pb(II) equilibrium was established only after 180 min at both the used temperatures and the reduction degree was lower and was equal to 52% at 283 K and 55% at 293 K. In the studies by Reczek at al. [40] the equilibrium of the Pb(II) sorption on the Norit carbon at the temperature 283 K is established after 90 min. The 4-CP slows down the process of the Pb(II) sorption on the used activated carbon.

Two of the most widely used kinetic equations for sorption are Lagergren's pseudo-first-order model and pseudo-second-order model. These models are based on the assumption that the sorption rate is proportional to the number of free sites on the surface of the sorbent, respectively to the first and second power. Table 1 shows the fitting of the kinetic models to the experimental data. The plotted

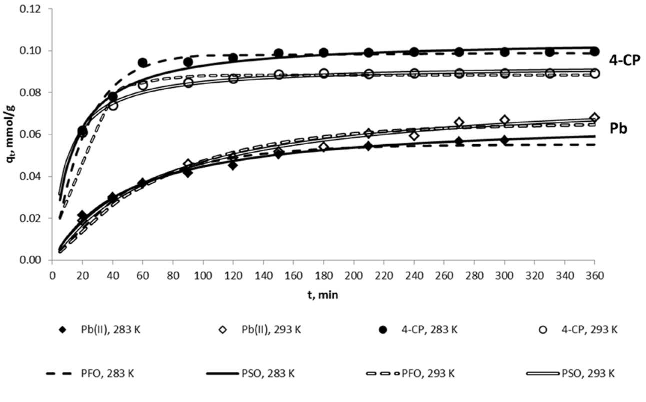

Fig. 1. The models of the pseudo-first-order (PFO) and pseudo-second-order (PSO) equation for the Pb(II) and the 4-CP onto Norit ROW 0.8 Supra carbon.

Table 1
The values of kinetic models constants for the sorption of Pb(II) and 4-CP onto Norit ROW 0.8 Supra carbon at 283 and 293 K

		Pb(II)		4-CP	
		Temperature, *K*		Temperature, *K*	
Model	Parameter	283	293	283	293
Pseudo-first order	q_e, mmol·g^{-1}	0.06	0.07	0.10	0.09
	k_1, min^{-1}	0.018	0.013	0.045	0.053
	R^2	0.9654	0.9660	0.9710	0.9530
Pseudo-second order	q_e, mmol·g^{-1}	0.07	0.08	0.11	0.09
	k_2, mmol·g^{-1} min^{-1}	0.294	0.171	0.714	1.106
	R^2	0.9867	0.9854	0.9807	0.9704
Weber-Morris model					
First linear portion	t, min	0–360	0–360	0–60	0–60
	k_{1d}, mmol·g^{-1}·min$^{-0.5}$	0.03	0.03	0.01	0.007
	c, mmol·g^{-1}	0.01	0.01	0.02	0.03
	R^2	0.9739	0.9740	0.9938	1.0
Second linear portion	t, min	–	–	60–360	60–360
	k_{2d}, mmol·g^{-1}·min$^{-0.5}$	–	–	0.0005	0.0005
	c, mmol·g^{-1}	–	–	0.09	0.08
	R^2	–	–	0.7877	0.7331

results obtained on the basis of these models using non-linear regression are presented in Fig. 1. Both the sorption of the Pb(II) ions and the 4-CP on the studied activated carbon followed the pseudo-second-order kinetic model. The coefficients of determination R^2 were higher for the pseudo-second-order kinetic model than the pseudo-first-order by Lagergren for the sorption of the Pb(II) and the 4-CP at both temperatures. The R^2 coefficient values amounted to 0.9867; 0.9854 for the Pb((II) at 283 K and 293 K and 0.9807; 0.9704 for the 4-CP at a temperature of 283 and 293 K, respectively. The experimental data fitted very well to the pseudo-second-order kinetic model which shows the chemical nature of the sorption process of the Pb(II) and the 4-CP from a bicomponent solution on the tested activated carbon. The pseudo-second-order kinetic model assumes that the ion exchange could take place between the sorbent and sorbate [33]. The functional groups are responsible for the ability of the ion exchange on the surface of the granular activated carbon. The rate constant k_2 had higher values in the case of the 4-CP sorption than the Pb(II). With the increased temperature in the case of the 4-CP the value of coefficient k_2 increases from 0.714 to 1.106 mmol·g^{-1}·min^{-1}, which means that the sorption of 4-CP proceeds faster at a higher temperature. In contrast, in the case of the Pb(II) sorption, the coefficient k_2 decreases insignificantly at the temperature 293 K from 0.294 to 0.171 mmol·g^{-1}·min^{-1}. This may likely be associated with the longer time it takes to establish a state of dynamic equilibrium in the case of the Pb(II) sorption on used granular activated carbon.

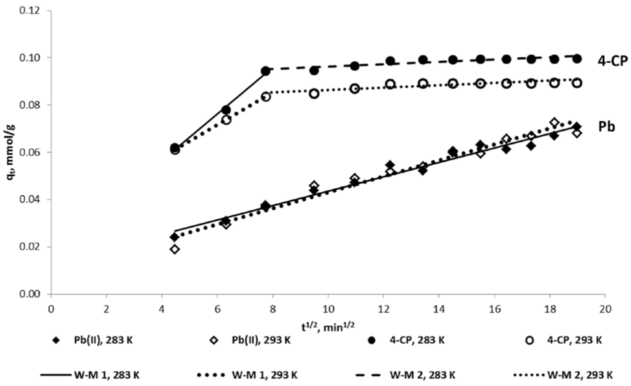

Fig. 2. The intraparticle diffusion plots for the Pb(II) and 4-CP sorption onto the Norit ROW 0.8 Supra carbon (W-M 1 – Weber-Morris model first portion, W-M 2 – Weber-Morris model second portion).

The Weber-Morris model of intraparticle diffusion can be represented on a graph $q_t = f(t^{0.5})$ (Fig. 2). The visible straight sections illustrate the multi-stage process of the sorption and the corresponding factors limiting its course in the various stages of the process (respectively the outside diffusion by the boundary liquid film on the surface of the sorbent grains, the intraparticle diffusion and then the step connected with establishing a state of equilibrium). The kinetic parameters of the Weber-Morris equation are shown in Table 1. In Fig. 2 the results of the Pb(II) and the 4-CP sorption on the Norit granular activated carbon at the temperatures of 283 and 293 K fitted into the Weber-Morris intramolecular diffusion model are shown. At both temperatures for the sorption of the Pb(II), one can extract only one range of linearity in the diagram. In the case of the 4-CP sorption, one can distinguish two ranges of linearity. In all of the cases, the value *c* determined for the first segment is greater than zero, which indicates that the primary factor limiting the rate of the process has not been intraparticle diffusion, but diffusion through the boundary film on the surface of the grains of the carbon. The greater the value *c*, the higher is the influence of diffusion through the boundary film on the surface of the sorbent grains is. The higher values of the coefficient c determined for the 4-CP sorption at both temperatures compared to the coefficient c determined for the Pb(II), testify to the fact that the external diffusion had an impact on the slowdown sorption of the Pb(II).

3.2. Sorption isotherms

For the modeling of the sorption equilibrium data, the Langmuir (Eq. 6), Freundlich (Eq. 7), Redlich–Peterson (Eq. 8) and Langmuir–Freundlich (Eq. 9) equations were examined. The values of the coefficients of the equations of the Pb(II) and 4-CP sorption isotherms on the granular activated carbon are shown in Table 2.

The fit of the sorption models to the experimental data of the Pb(II) and the 4-CP is very high, the coefficients of determination R^2 reached levels 0.9616–0.9983. The sorption of Pb(II) on the Norit granular activated carbon is best described by the isotherm equations of the Langmuir–Freundlich (R^2 = 0.9914, 283 K) and Redlich–Peterson (R^2 = 0.9951, 293 K). Likewise, in the case of the sorption of 4-CP on the Norit granular activated carbon is best described by the isotherm equations of the Langmuir–Freundlich (R^2 = 0.9983, 283 K) and Redlich–Peterson (R^2 = 0.9915, 293 K). Both in the case of the Pb(II) and the 4-CP the low values of R^2 predicted by Langmuir isotherm model does not represent on sorption behavior.

The constant q_m of the Langmuir isotherm allows the estimation of the maximum sorption capacity, i.e., the maximum amount of the sorbate required to fill a monolayer. It is approximately five times greater for the 4-CP than for the Pb(II). In the case of the Pb(II), the maximum sorption capacity is very similar at both temperatures. In the case of the 4-CP at a temperature of 293 K it is about 0.18 mmol·g^{-1} higher. Using the Eq. (11) [41] the maximum sorption capacity of the Freundlich equation can be calculated:

$$K_F = \frac{q_{mF}}{C_0^{1/n}} \tag{11}$$

The values of q_{mF} are presented in Table 2. In the case of the Pb(II), practically the same values as q_m were obtained from the Langmuir equation. The calulated value of q_{mF} for the 4-CP from the Eq. (11) is greater than obtained from the Langmuir equation, at both of the used temperatures, probably because that in the case of the 4-CP sorption, it is better described by the isotherm equations of the Redlich–Peterson, Ferundlich and Langmuir–Freundlich models.

Reczek et al. [40] analyzed the Pb(II) sorption on granular activated carbon Norit from a solution of the single-component and obtained a maximum sorption capacity of Pb(II) of 0.09 mmol/g. This value is comparable to that obtained in this study.

The equilibrium parameter, R_L defined by Eq. (12) [41] determines the nature of the sorption:

$$R_L = \frac{1}{1 + b \cdot C_0} \tag{12}$$

The value of this parameter may be used to predict whether the sorption system is preferred. At both the used temperatures, for the Pb(II) as well as the 4-CP this parameter is in the range <0; 1>, (0.04 – 0.41 for Pb(II) and 0.04 – 0.23 for 4-CP), which means that the sorption of the used pollutants on the granulated activated carbon has a positive character.

The magnitude of the Freundlich isotherm exponent n gives an indication of the favourability of the sorption. It is generally stated that the values of n in the range 2–10 represent good, 1-2 moderately difficult, and less than 1 poor sorption characteristics [42]. The Norit activated carbon is a good sorbent for Pb(II) and 4-CP at both temperatures (2.68< n <3.35).

Table 2
Constant values of isotherm models for Pb(II) and 4-CP onto Norit activated carbon at 283 and 293 K

		Pb(II)		4-CP	
		Temperature, *K*		Temperature, *K*	
Model	Parameter	283	293	283	293
Langmuir	q_m, mmol·g^{-1}	0.11	0.08	0.48	0.66
	b, L·mmol^{-1}	6.27	31.54	25.38	13.84
	R^2	0.9784	0.9785	0.9943	0.9616
Freundlich	K_F(mmol·g^1)(L·mmol^{-1})$^{1/n}$	0.10	0.11	0.80	0.85
	n	3.27	3.35	2.68	2.75
	R^2	0.9831	0.9869	0.9959	0.9915
	q_{mF}	0.09	0.10	0.78	0.83
Redlich–Peterson	A, L·g^{-1}	3.13	9.37	177.90	147.44
	B, L·mmol^{-1}	28.41	93.10	232.83	198.64
	g	0.68	0.77	0.65	0.70
	R^2	0.9663	0.9951	0.9977	0.9915
Langmuir–Freundlich	q_{mLF}, mmol·g^{-1}	0.24	0.15	1.30	2.49
	K_{LF}, L·mmol^{-1}	0.37	3.77	1.10	0.24
	m_{LF}	0.41	0.46	0.47	0.47
	R^2	0.9914	0.9902	0.9983	0.9882

The Redlich–Peterson isotherm is an empirical isotherm incorporating three parameters. It combines elements from both the Langmuir and Freundlich equations and the mechanism of sorption is a hybrid so does not follow the ideal monolayer sorption. At high liquid-phase concentrations of the sorbate Eq. (8) reduces to the Freundlich equation (Eq. 13):

$$q_e = \frac{A}{B} C_e^{1-g} \tag{13}$$

where *A*/*B* and *(1-g)* present, respectively, the parameters K_F and *1/n* of the Freundlich model. For $g = 1$, Eq. (8) reduces to the Langmuir equation, where $b = B$ is the Langmuir sorption constant related to the energy of sorption and $A = bq_m$, where q_m = signifies the Langmuir maximum sorption capacity of the sorbent. For $g = 0$, the Redlich–Peterson equation reduces to Henry's equation [37]. A harmony is found between the ratio *A*/*B* of the Redlich–Peterson model and the constant K_F of the Freundlich equation also for the parameter *1/n* of the Freundlich model and the term *(1-g)*. *A*/*B* calculated for the Pb(II) and the 4-CP at 283 and 293 K, respectively, 0.11; 0.10; 0.76; 0.74 and the term *(1-g)*, respectively, 0.32; 0.23; 0.35; 0.30.

Both in the case of the Pb(II) and the 4-CP sorption, the values of the maximum sorption capacity obtained using the Langmuir–Freundlich equation are higher than those calculated by the Langmuir and Freundlich models. This indicates that, according to the Langmuir–Freundlich isotherms, the Pb(II) and 4-CP are not sorbed evenly on the sorbent surface. An agreement is obtained between the parameter m_{LF} and the constant *1/n* of the Freundlich equation.

3.3. Thermodynamic parameters

In environmental engineering practice, both the energy and entropy factors must be considered in order to determine what processes will occur spontaneously. Gibb's free energy change, ΔG°, is the fundamental criterion of spontaneity. The reaction occurs spontaneously at a given temperature if ΔG° is a negative value. The thermodynamic parameter, ΔG°, is shown in Table 3.

The negative values of the free energy obtained in the sorption of both Pb(II) and 4-CP indicate that the sorption could be spontaneous. The decrease of the ΔG° value with an increase in the temperature (–4.32 up to –8.41 kJ·mol^{-1}) implies a larger spontaneity of the Pb(II) sorption process at higher temperatures. The increase of the ΔG° value with an increase in the temperature (–7.61 to –6.40 kJ·mol^{-1}) implies a lower spontaneity of the 4-CP sorption process at higher temperatures.

Table 3
Thermodynamic parameters for the sorption of Pb(II) and 4-CP onto Norit activated carbon

	ΔG°, kJ·mol^{-1}	
	283 K	293 K
Pb(II)	–4.32	–8.41
4-CP	–7.61	–6.40

4. Conclusion

The selected sorbates Pb(II) and 4-CP are often present in water pollutants. In this work it has been shown, that the investigation of the simultaneous sorption of various chloro-organics and heavy metal ions from an aqueous solution on activated carbon is possible in the proposed manner. The equilibrium of the 4-CP sorption on granular activated carbon (Norit ROW 0.8 Supra) was established faster than the Pb(II) sorption. The presence of the 4-CP slowed down the Pb(II) sorption. Both the sorption of the Pb(II) ions and the 4-CP at temperatures 283 and 293 K followed the pseudo-second-order kinetic model. It shows the chemical nature of the sorption process of the Pb(II) and 4-CP from a bicomponent solution on the tested activated carbon. The primary factor limiting the rate of the 4-CP and Pb(II) sorption has not been the intraparticle diffusion, but the diffusion through the boundary film on the surface of the grains of the carbon, as well as the external diffusion which had an impact on the slowdown sorption of the Pb(II). The sorption equilibrium of both the Pb(II) and the 4-CP at 283 K on the Norit granular activated carbon was best described by the Langmuir–Freundlich isotherm equation. At a temperature of 293 K, the sorption of the Pb(II) was best described by the Redlich–Peterson isotherm equation ($R^2 = 0.9951$), but in the case of the 4-CP, the sorption was best described by both the Redlich–Peterson and Freundlich models. The maximum amount of 4-CP sorbed on the activated carbon was about five times greater than the amount of Pb(II) sorbate (calculated using the Langmuir model). The maximum sorption capacities of the Pb(II) and the 4-CP obtained using the Langmuir–Freundlich equation are higher than those calculated by the Langmuir and Freundlich models, which indicates that, the sorbates are not sorbed evenly on the sorbent surface. The sorption of the 4-CP and the Pb(II) on the granulated activated carbon has a positive character and is favourable. The sorption process occurred spontaneously. An increase in the temperature resulted in a growth of the spontaneity of the Pb(II) sorption and a decrease in the spontaneity of the 4-CP sorption.

Symbols

4-CP	—	4-chlorophenol
Pb(II)	—	Lead(II)
C_0	—	Initial concentrations Pb(II)/4-CP, mmol·L^{-1}
C_e	—	Equilibrium concentrations Pb(II)/4-CP, mmol·L^{-1}
C_t	—	Concentrations Pb(II)/4-CP at time t, mmol·L^{-1}
m	—	Activated carbon mass, g
V	—	Volume of sample, L
q_e	—	Amount of sorption at equilibrium, mmol·g^{-1}
q_t	—	Amount of sorption at time *t*, mmol·g^{-1}
k_1	—	Rate constant of pseudo-first-order sorption process, min^{-1}
k_2	—	Rate constant of pseudo-second-order sorption process, g·mmol^{-1}·min^{-1}
t	—	Time, min
k_{id}	—	Weber-Morris kinetic constants, mmol·g^{-1}·min$^{-0.5}$
c	—	Intercept from Weber-Morris equation, mmol·g^{-1}

q_m — Langmuir isotherm constant, mmol·g^{-1}
b — Langmuir isotherm constant, L·mmol^{-1}
K_F — Freundlich isotherm constant, (mmol·g^{1}) (L·mmol^{-1})$^{1/n}$
n — Freundlich isotherm constant
A — Redlich–Peterson isotherm constant, L·g^{-1}
B — Redlich–Peterson isotherm constant, L·mmol^{-1}
g — Redlich–Peterson isotherm constant
q_{mLF} — Langmuir–Freundlich isotherm constant, mmol·g^{-1}
m_{LF} — Langmuir–Freundlich isotherm constant, L·mmol^{-1}
R^2 — Determination coefficient
R — Universal gas constant, 8.314 J·mol^{-1}·K^{-1}
T — Absolute temperature, K
q_{mF} — The maximum sorption capacity of the Freundlich equation
R_L — Equilibrium parameter

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