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Effect of lead(II) presence on sorption of 4-chlorophenol on synthetic activated carbon

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ABSTRACT

In the presented study, sorption kinetics of 4-chlorophenol (4-CP) from one-component (S1) and two-component (S2) aqueous solutions is investigated and described. S1 is 4-CP solution, S2 is a solution of 4-CP and lead(II). Synthetic activated carbon AF5 was used as a sorbent. Sorption process was carried out at 10°C, 15°C, 20°C, and 25°C. In analysis of the findings sorption and diffusion kinetic models were used. In order to investigate the mechanism of 4-CP sorption pseudo-first order (PFO), pseudo-second order (PSO), Elovich (E) kinetic models were used. In order to determine the rate controlling step of 4-CP sorption, liquid film diffusion (LFM), and intraparticle diffusion kinetic (IPD) models were used. 4-CP sorption in the presence of lead(II) and in the absence of this component follows the PSO model, suggesting the chemical nature of the process. The speed of the 4-CP sorption process on AF5 activated carbon without and in the presence of lead(II) is influenced by diffusion through the boundary layer and intraparticle diffusion.

Keywords: 4-CP removal; Lewatit AF5; Pseudo-first order; Pseudo-second order; Elovich; Liquid film diffusion; Intraparticle diffusion kinetic models

1. Introduction

Chlorophenols are a group of phenolic compounds with chlorine atoms attached to the phenolic ring. Chlorophenols differ between each other with the setting of chlorine atoms in phenol molecule. In case of 4-CP, which in room temperature takes form of white or pink little needles, chlorine's atom is in fourth position. Chlorophenols dissolve well in organic solvent, and worse in water. Despite the poor solubility in water, they occur in ground water, earth water and in the one designed to be drinkable for humans [1,2].

Chlorophenols are ubiquitous contaminants in the environment primarily released from agricultural and industrial wastewater. The principal source of water pollution is pharmaceutical industry, petrochemical industry, plastic production plants and plant protection product plants. Chlorophenols are used as inter alia biocides, wood maintenance products, pesticides. Chlorophenols are also formed in sewage treatment plants and water treatment stations where chlorination processes are used. Chlorophenols in drinkable water worsen its taste and scent. Unpleasant, galling,

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distinctive, often described as pharmaceutical taste and scent of those compounds can be perceptible in water even on level 0.01 mg/L [2]. Chlorophenols belong to compounds with perilous impact on natural environment. These compounds are not readily degraded naturally, and easily accumulate in organs, tissues and cells via food chains, further leading to acute and chronic toxic effects on aquatic organisms [3]. Due to toxic properties chlorophenols are found on the list of priority substances in the field of water policy European Communities [4] and are recognized as a priority pollutant by the United States Environmental Protection Agency (USEPA).

The removal of chlorophenols from water has been the subject of research for several years. Many technologies have been applied for the removal of chlorophenolic compounds in aqueous phase, including advanced oxidation processes, biological processes, electrochemical oxidation, reverse osmosis, and adsorption process, which is the focus of researchers [5–7]. A variety of adsorbents have been used for the adsorption of chlorophenols from aqueous solutions such as activated carbon [8,9], nanotubes [10], peat [11], or silica materials [12]. Activated carbon is considered as the most effective material for the adsorption of phenolic compounds from water and wastewater.

Lead is one of the most abundant heavy metals in the environment. The major source of lead contamination is the wastewater from process industries engaged in lead acid battery, paints, oils, electronic production and also combustion of fossil fuel, forest fires, and mining activity. Lead is one of more toxic metals, which is connected to i.a. its accumulation in living organisms [13]. Rated as a substance particularly harmful to water environment, its concentration should be limited [14].

There are many methods of elimination of heavy metals, i.a. lead from water and sewage. For heavy metals' removal from water mainly physicochemical methods are used: chemical loss, coagulation, membrane processes, ion exchange, dissolvent extraction. Conventional methods of heavy metals' removal are not suitable for purifying large amounts of water with low concentration of unwelcome components, their usage in those conditions is energy intensive and leads to formation of great amount of secondary pollution, therefore most commonly used method of elimination of heavy metals i.a. lead is sorption [15].

Analysis of heavy metals' sorption i.a. lead on active carbons was conducted in researches [16–20]. Efficiency of sorption was high and amounted to 80%–90%. There were also researches conducted on usage of lead in adsorption process of mineral materials i.a. diatomite, dolomite, perlite [21], clinoptilolite [16,22], chalcedonite modified with manganese oxide [16] as sorbents. All materials worked well as lead sorbents. Studies on biosorption of lead and other heavy metals were also conducted in wide range [23,24].

Kinetic studies, next to isotherms and thermodynamic studies, play an important role in thoroughly understanding the sorption process of organic and inorganic compounds in water solutions. Predicting the rate at which the pollutants removal takes place in a given solid/solution system is one of the most crucial factors for the effective sorption system design. Compared with the extensive separate studies on the sorption of heavy metals or organic contaminants in water and wastewater, there is little information on the effect of heavy metals on the sorption of organic contaminants and vice versa [20,25–27]. However, it should be realized that chlorophenols and heavy metals may occur together in water or wastewater. Therefore, it is very important to study the sorption behaviours of organic contaminants in the presence of heavy metals. The aim of the present study was to investigate the sorption kinetics of 4-CP on synthetic activated carbon AF5 as affected by lead. Scope of research included experiments of sorption kinetics 4-CP on AF5 with and without lead at a temperature in the range of 10°C–25°C, which is distinctive for natural waters environment. In analysis of findings, sorption and diffusion kinetic models were used.

2. Materials and methods

2.1. Preparation of sorbent and solutions

As sorbent synthetic activated carbon was used, commercial product called Lewatit AF5. Synthetic carbon material AF5 has monospheric form. On the surface of black granules, elongated gaps are found, visible on microphotography in Fig. 1a. AF5 is microporous material; the size of specific area, and volume of micropores and mesopores of which is determined on the basis of isotherms of nitrogen's adsorption/desorption amount to, respectively, 1,250 m^2/g, 0.6 cm^3/g, 0.040 cm^3/g [28]. The elemental composition of AF5 was determined using the energy X-ray analysis (EDX, Fig. 1b), which showed the presence of C (97.53%) and O (2.47%).

In experiment, two kinds of solutions S1 and S2 in separate research series were used. One-component S1 is 4-CP solution with permanent initial concentration amounted to approximately 70 mg/L (0.55 mmol/L). Two-component S2 is a solution of 4-CP and lead(II). Concentration of 4-CP in S2 similar to S1 reached about 70 mg/L (0.55 mmol/L). Concentration of lead(II) in S2 amounted to approximately 100 mg/L (0.45 mmol/L). In double-distilled water 4-CP implemented in solid form as white crystals, lead as lead nitrate (V) salt ($Pb(NO_3)_2$), which after dissolution formed researched solutions.

2.2. Sorption kinetics experiment

In conical flasks, aliquots of AF5 material weighing 0.15 g were prepared with analytical scales Kern ABT 220–4 M of reading accuracy of 0.0001 g. To each of the flasks, 50 mL of solution were poured S1 and S2 for given research series, respectively. Samples were placed in thermostatic shaker and exposed to shaking at 160 rpm at 10°C, 15°C, 20°C, and 25°C. Samples of sorbates were taken away after time *t* equal to 10, 20, 30, 40, 60, 90, 120, 150, and 180 min.

The concentration of 4-CP in solutions before and after sorption was expressed through designation of overall content of organic carbon (TOC). The amount of TOC in water is direct scale of quantity of organic compounds. TOC was measured in solutions with automatic analyser of organic carbon IL550 Hach Lange (USA). The concentration of lead(II) in S2 solution was measured with atomic absorption spectrometer 990 of PG Instruments (UK), using flame atomization technique at wavelength 217.0 nm. Throughout the research, pH of each analysed sample was monitored. For pH measurement Sension Direct 200 pH-meter (Hach, USA) with gel electrode was used.

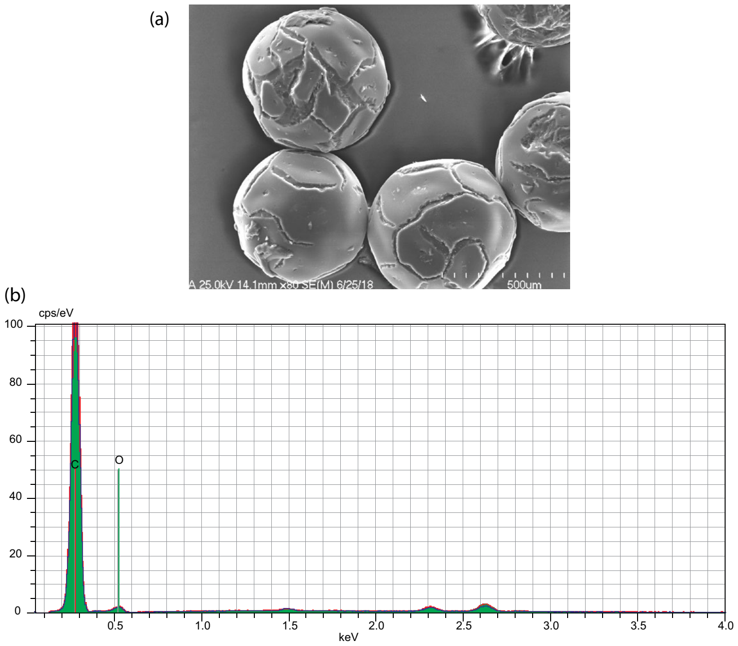

Fig. 1. (a) SEM micrographs of AF5 and (b) EDX of AF5.

Sorption capacity in time q (mg/g) was calculated with use of Eq. (1):

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

where C_0, C_t – initial and equilibrium concentration of 4-CP at time t, mg/L; m – AF5 mass, g; V – volume of sample, L.

The removal efficiency of 4-CP (%) was calculated with use of Eq. (2):

$$\text{RE}=\frac{C_0-C_e}{C_0}\cdot 100\% \tag{2}$$

where C_e – equilibrium concentration of 4-CP, mg/L.

2.3. Modelling

In order to investigate the mechanism and to determine the rate controlling step of sorption of 4-CP, pseudo-first order, pseudo-second order, Elovich, liquid film diffusion model (LFM) and intraparticle diffusion kinetic models were used.

Pseudo-first order (PFO) model described by equation in general formula [29]:

$$q=q_e\left(1-e^{-k_1t}\right) \tag{3}$$

and linear form:

$$\ln\left(q_e-q\right)=\ln q_e-k_1t \tag{4}$$

where q_e – amount of sorption at equilibrium, k_1 – rate constant of PFO model, t – time, min.

Pseudo-second order model (PSO) described by equation in general formula [30]:

$$q=\frac{q_e^2k_2t}{1+q_ek_2t} \tag{5}$$

and linear form:

$$\frac{t}{q}=\frac{1}{k_2q_e^2}+\frac{1}{q_e}\cdot t \tag{6}$$

where k_2 – rate constant of PSO model.

Elovich model (E) [31] is described by equation in general formula [32]:

$$q=\frac{1}{b}\ln\left(1+ab\cdot t\right) \tag{7}$$

and linear form:

$$q=\frac{1}{b}\ln t+\frac{1}{b}\ln ab \tag{8}$$

where a – initial sorption rate, b – desorption constant related to the extent of surface coverage and activation energy for chemisorption.

LFM [33] is applicable at slow process of adsorbate flow through the liquid film surrounding the adsorbent particles, which determines the kinetics of the process. The mathematical form of LFM is given by:

$$\ln\left(1-F\right)=-k_{\text{fd}}\cdot t \tag{9}$$

where $F = q/q_e$ – fractional attainment of equilibrium, and k_{fd} – film diffusion rate constant.

The intraparticle diffusion model (IPD) [34] is expressed as:

$$q = k_i t^{1/2} + c \tag{10}$$

where k_i (mg/g min$^{1/2}$) is intraparticle diffusion rate constant with c as intercept along q axis.

Their validities can be determined by the calculation of the standard deviation (SD) Δq, and the coefficient of determination R^2. The best-fit model is the one with the lowest value of SD and the one in which the value of R^2 is closer to unity. The expression of SD equation is given as follows:

$$\Delta q = \sqrt{\frac{\sum\left[\left(q_{\text{exp}} - q_{\text{cal}}\right) / q_{\text{exp}}\right]^2}{N-1}} \tag{11}$$

where q_{exp} and q_{cal} – experimental and calculated sorption capacities, and N – number of data points.

3. Results and discussion

In Fig. 2, the impact of contact time on equilibrium concentration of 4-CP in S1 and S2 solutions at 10°C, 15°C, 20°C, and 25°C is shown. The equilibrium of dynamic sorption 4-CP on AF5 from one-component solution S1 established itself after 90 min in all researched temperatures, while in S2 solution after approximately 120 min. During the first 40 min, process of 4-CP sorption from S1 and S2 solutions on AF5 sorbent in all researched temperatures proceeded quickly because of high accessibility of active space on sorbent's surface. Presence of heavy metal had impact on organic compound adsorption on AF5's surface. Similar time of reaching equilibrium of 4-CP sorption from two-component solution (60–90 min) was obtained during other researches [20].

Table 1 is showing the effectiveness of 4-CP removal from S1 and S2 at 10°C, 15°C, 20°C, and 25°C during time of establishing equilibrium, that is, after 90 min in S1 and 120 min in S2. Removal efficiency of 4-CP calculated according to Eq. (2) in S1 was contained in compartment 80.4–86.8, in S2 was slightly lower and in compartment of 79.6–83.9. The presence of lead(II) in S2 solution decreased the percentage of 4-CP removal. Along with temperature rising in both solutions, the effectiveness of 4-CP removal was higher.

pH value of solutions after sorption in S1 sets oscillated between 7.00 and 9.00, which means neutral and slightly alkaline environment. In S2 sets, pH value amounted to 5.50–6.50, that is, the reaction was slightly acidic. Lower pH value in S2 sets was determined by adding salt $Pb(NO_3)_2$ hydrolysed in water to weak base and strong acid HNO_3 that acidified the environment. The logarithmic acid dissociation constants

Table 1
Effectiveness of 4-CP removal (RE) from S1 and S2 at 10°C, 15°C, 20°C, and 25°C during time of establishing equilibrium (S1 – 90 min; S2 – 120 min)

Temperature, °C	RE, %	
	S1	S2
10	80.4	79.6
15	83.5	82.7
20	84.9	83.8
25	86.8	83.9

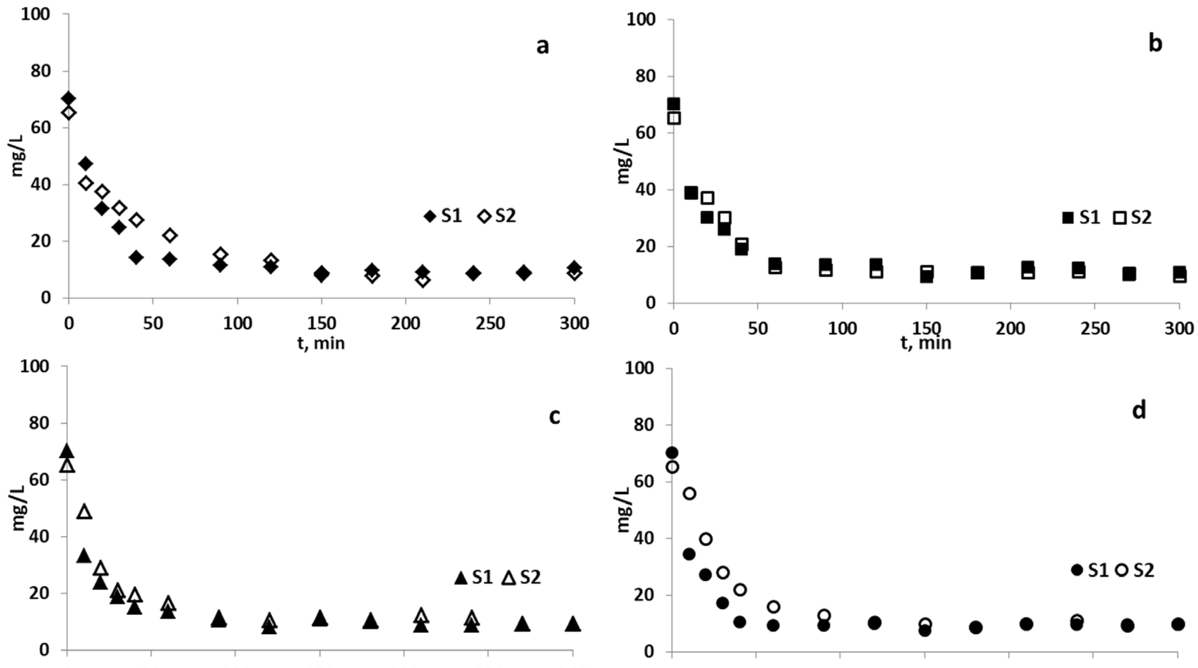

Fig. 2. Effect of contact time on concentration of 4-CP on S1 and S2, (a) 10°C, (b) 15°C, (c) 20°C, and (d) 25°C.

pK_a of 4-CP amounted to 9.47 [35]. The process of sorption of 4-CP from solutions held in lower pH than it's pK_a. In this case organic compound remained in non-ionised form and electrostatic interactions have not impacted its adsorption. Therefore the conclusion is that if 4-CP occurred in S2 as molecule and presumably was adsorbed pursuant to molecule mechanism, no contest took place between chlorophenol and lead sorbed most likely according to ion exchange reaction. Similar relationships were shown in researches [36,37].

In order to investigate the mechanism of sorption of 4-CP on AF5 from S1 and S2, PFO, PSO, and Elovich kinetic models were used. Table 2 shows breakdown of characteristic parameters of PFO, PSO, and Elovich models in linear and general formula, value of R^2 determination factor and standard Δq deviation of 4-CP sorption from S1 and S2 on AF5 sorbent at 10°C, 15°C, 20°C, and 25°C. The process of models is shown in Fig. 3.

High values of R^2 determination factor received for PFO, PSO, and Elovich models (Table 2) show that used models describe the collected data well. Highest values of R^2 determination factors – better fitting of experimental data of 4-CP sorption from S1 solution, were received for linear form of PSO model. In case of sorption from S2 solution only at 25°C better fitting of experimental data of 4-CP sorption was received for PFO in general formula, for remaining temperatures the best fitting of data was collected in linear form of PSO. While analysing values of standard Δq deviation for kinetic models of 4-CP sorption from S1 and S2 on AF5 low values of Δq obtained for PSO model order show better fitting of experimental data for pseudo-second order kinetic model. The pseudo-second order kinetic model assumes the chemical character of sorption [38]. This suggested that the overall rate of the sorption of 4-CP from one-component S1 and from S2 on AF5 was controlled by chemisorption. Similar phenomena have been observed in the sorption of 4-CP on activated carbon prepared from rattan sawdust [39], granular activated carbon [20,40], and nanotubes [35,40].

The plots of Elovich model with good R^2 values over 0.8, for S1 in the range 0.8068–0.9331 and for S2 0.8412–0.9850 suggest that the sorption process of 4-CP from S1 and S2 on AF5 follows the pseudo-second order kinetic model based on the assumption that the rate determining step may be chemisorption [39].

Fig. 4a shows relationship between constant k_2 and temperature of sorption's conduction in researched 4-chlorophenol solutions. It is noticeable that in both S1 and S2 cases value of constant k_2 of PSO model does not depend on temperature. Trend lines $k_2 = f(\text{temperature})$ are parallel on the OX axis.

Relationship between speed of constant k_2 and temperature can be described with Arrhenius equation with linear formula written below [41]:

$$\ln k_2 = \ln A - \frac{E_a}{R}\left(\frac{1}{T}\right) \tag{12}$$

where A is a temperature independent factor, having the same unit as k_2, g/(mg min), E_a is the activation energy of adsorption, J/mol; R is the ideal gas constant (8.314 J/mol K), and T is the solution temperature, K. Relationship between speed of constant k_2 of PSO model and temperature of 4-CP sorption on AF5 from S1 and S2 is shown in Fig. 4b. High values of R^2 coefficient received 0.9561 and 0.9616, respectively, for S1 and S2 based on Arrhenius equation allow to calculate sorption of 4-CP from S1 and S2 on AF5 activation energy values. Those values amounted to 45.3 and 28.8 kJ/mol for S1 and S2, respectively, and correspond to chemical sorption activation energy values. Chemical adsorption activation energy fits in the range between 8 and 84 kJ/mol, value of activation energy for physical adsorption is usually lower than 4 kJ/mol since in case of physical adsorption the system quickly reaches equilibrium [42,43]. The above leads to the conclusion that 4-CP sorption from one-component S1 solution as well as from two-component S2 solution on AF5 sorbent is a chemical sorption.

Wu et al. [44] defined approaching equilibrium factor in the PSO model (R_w) in formula:

$$R_w = \frac{1}{1 + k_2 q_e t_{\text{ref}}} \tag{13}$$

where t_{ref} – longest time of sorption process, min. Table 2 summarizes the values of the R_w coefficient for the kinetic model of the pseudo-second order of sorption 4-CP on AF5 from solutions S1 and S2 at temperatures 10°C, 15°C, 20°C, and 25°C. The values of the R_w factor of the PSO model are in the range $0.1 > R_w > 0.01$. Achieving the equilibrium of the considered sorptive–sorbent system is not difficult. The values of the coefficient R_w of the sorptive system S1–sorbent AF5 decrease with increasing temperature and are, respectively, 0.08, 0.06, 0.04, and 0.04 at 10°C, 15°C, 20°C, and 25°C. This allows to conclude that as the temperature rises, achieving the equilibrium state of the sorption system S1–sorbent AF5 is faster. The values of the R_w factor for the sorptive system S2–sorbent AF5 are 0.12, 0.09, 0.08, and 0.13 at 10°C, 15°C, 20°C, and 25°C, respectively. Comparing the values of the R_w factor of sorption systems S1-AF5 and S2-AF5 at the same temperatures, it can be seen that for the S2-AF5 system the R_w values are higher, close to 0.1. For $1 > R_w > 0.1$, achieving equilibrium is difficult [44]. On this basis, it can be concluded that in the case of the 4-CP and Pb(II) sorptive compared with the one-component sorptive, the conditions for achieving equilibrium deteriorate.

Wu et al. [45] defined approaching equilibrium parameter based on Elovich equation (R_E) with formula:

$$R_E = \frac{1}{q_{\text{ref}} b} \tag{14}$$

The values of the R_E coefficient summarized in Table 2 for the Elovich model of sorption 4-CP on AF5 with S1 and S2 at 10°C, 15°C, 20°C, and 25°C are in the range $0.3 > R_E > 0.1$, confirm the chemical nature of 4-CP sorption S1 and S2 on AF5. The R_E values obtained for S2 are higher at each test temperature than those obtained for S1, which confirms that sorption of 4-CP from the S2 two-component solution occurs more slowly than from the S1 one-component solution.

The initial sorption rate can be calculated by using the pseudo-second order model using the following expression [30]:

$$h = k_2 \cdot q_e^2 \tag{15}$$

Table 2
Kinetic parameters of PFO, PSO, and Elovich models for 4-CP sorption from S1 and S2 on AF5

PFO model	q_e, mg/g	k_1, 1/min	R^2	Δq		q_e, mg/g	k_1, 1/min	R^2	Δq	
	S1, 10°C					S2, 10°C				
Nonlinear	20.2	0.05	0.9824	0.035		18.5	0.032	0.9325	0.147	
Linear	20.0	0.06	0.9467	2.669		19.7	0.021	0.9822	0.274	
	S1, 15°C					S2, 15°C				
Nonlinear	19.3	0.06	0.9417	0.069		18.2	0.042	0.9301	0.118	
Linear	19.3	0.06	0.8337	1.814		18.2	0.042	0.9424	0.692	
	S1, 20°C					S2, 20°C				
Nonlinear	19.7	0.08	0.9288	0.049		18.1	0.048	0.9687	0.105	
Linear	20.2	0.07	0.8865	3.117		18.3	0.048	0.7735	0.917	
	S1, 25°C					S2, 25°C				
Nonlinear	20.4	0.07	0.9489	0.055		18.8	0.032	0.9816	0.224	
Linear	20.7	0.04	0.8039	3.425		19.0	0.026	0.9870	0.402	
PSO model	q_e, mg/g	k_2, g/(mg min)	R^2	Δq	R_w	q_e, mg/g	k_2, g/(mg min)	R^2	Δq	R_w
	S1, 10°C					S2, 10°C				
Nonlinear	22.9	0.003	0.9492	0.082	0.08	21.2	0.002	0.9577	0.095	0.12
Linear	22.2	0.003	0.9964	0.086		21.7	0.002	0.9945	0.135	
	S1, 15°C					S2, 15°C				
Nonlinear	21.3	0.004	0.9764	0.031	0.06	20.6	0.003	0.9214	0.098	0.09
Linear	21.2	0.004	0.9983	0.031		20.1	0.003	0.9937	0.094	
	S1, 20°C					S2, 20°C				
Nonlinear	21.2	0.007	0.9835	0.018	0.04	20.7	0.003	0.9348	0.164	0.08
Linear	21.0	0.008	0.9989	0.026		20.1	0.003	0.9927	0.123	
	S1, 25°C					S2, 25°C				
Nonlinear	22.2	0.005	0.9287	0.048	0.04	22.2	0.002	0.9582	0.320	0.13
Linear	21.5	0.007	0.9983	0.062		22.3	0.001	0.9703	0.176	
Elovich model	a, mg/g min	b, g/mg	R^2	Δq	R_E	a, mg/g min	b, g/mg	R^2	Δq	R_E
	S1, 10°C					S2, 10°C				
Nonlinear	4.5	0.24	0.8578	0.1413	0.21	1.86	0.22	0.9850	0.053	0.23
Linear	4.7	0.24	0.8645	0.1317		2.37	0.24	0.9797	0.061	
	S1, 15°C					S2, 15°C				
Nonlinear	9.5	0.30	0.9315	0.0553	0.17	3.17	0.26	0.8881	0.097	0.22
Linear	9.8	0.30	0.9331	0.0540		3.54	0.26	0.8901	0.097	
	S1, 20°C					S2, 20°C				
Nonlinear	50.2	0.38	0.8936	0.0540	0.13	3.25	0.25	0.8412	0.231	0.22
Linear	50.3	0.38	0.8939	0.0538		3.36	0.25	0.8511	0.211	
	S1, 25°C					S2, 25°C				
Nonlinear	29.2	0.34	0.8068	0.0819	0.14	1.17	0.18	0.9009	0.377	0.30
Linear	29.2	0.34	0.8076	0.0815		1.42	0.19	0.9259	0.256	

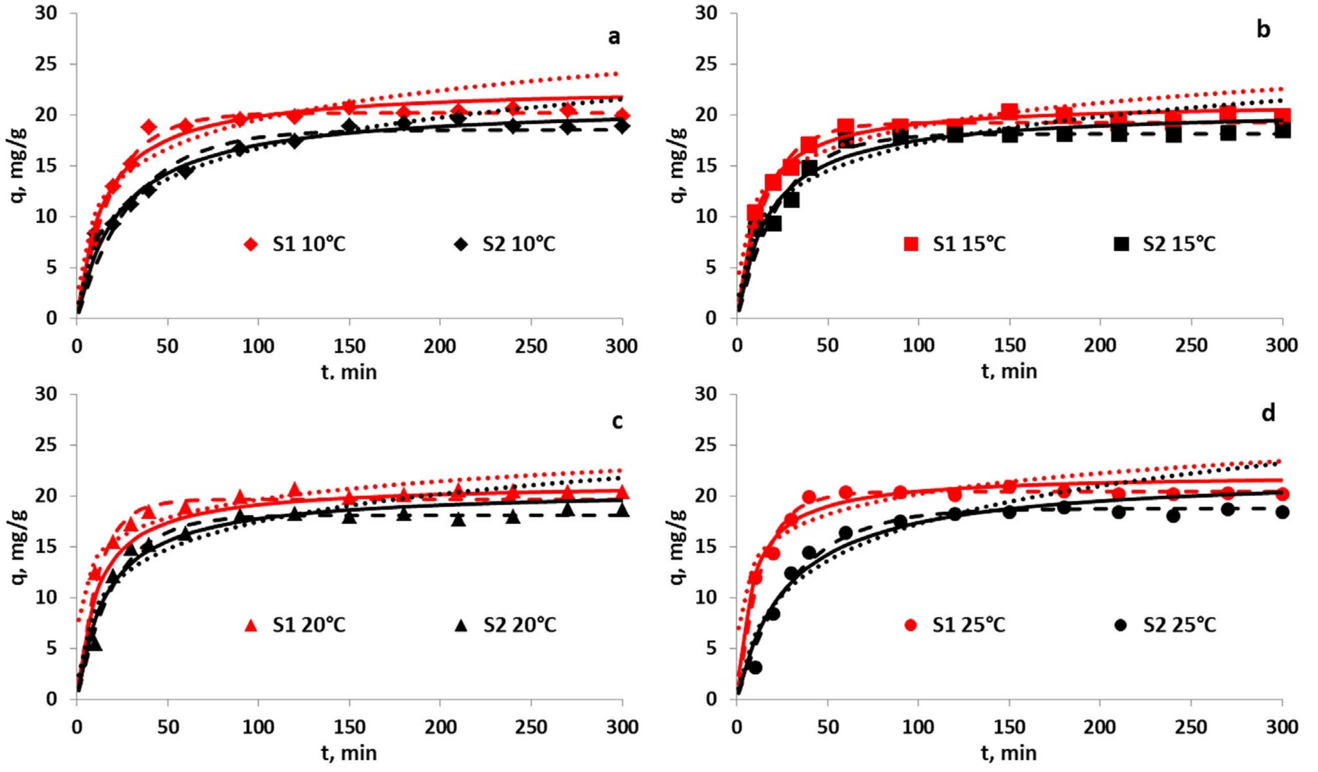

Fig. 3. Pseudo-first order (dashed line), pseudo-second order (solid line) and Elovich (dotted line) models for 4-CP sorption on AF5 with S1 and S2 solutions: (a) 10°C, (b) 15°C, (c) 20°C, and (d) 25°C.

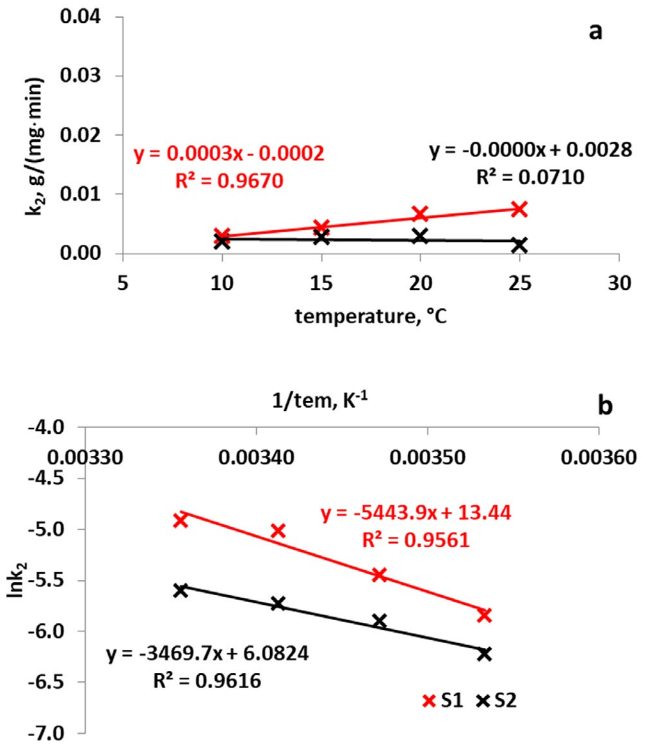

Fig. 4. (a) Plot of k_2 vs. temperature and (b) Arrhenius plot for the kinetic data.

The results give value for S1 (1.57, 1.81, 3.15, and 2.46 at 10°C, 15°C, 20°C, and 25°C) are higher at each test temperature than those obtained for S2 (0.90, 1.27, 1.28, and 0.98 at 10°C, 15°C, 20°C, and 25°C). The presence of lead(II) affects 4-CP sorption on AF5 synthetic activated carbon.

In order to determine the rate controlling step of sorption of 4-CP on AF5 from S1 and S2, LFM and IPDs were used. Liquid film diffusion model assumes that the slowest stage of the sorption process is diffusion through the boundary layer of the sorptive solution [33]. A linear plot of $(1 - q/q_e)$ vs. t with zero intercept suggests that adsorption kinetics is controlled by diffusion through liquid film surrounding the solid sorbents [46]. The k_{fd} was calculated from the slope of the straight line plot and its value along with R^2 is presented on Fig. 5. The close to unity value of R^2 0.7857–0.8584 for S1 and 0.8564–0.9237 for S2, respectively, indicated good fitness of film diffusion model. However, the straight lines did not pass through the origin thereby suggesting that film diffusion might not be the sole rate-limiting step.

The mass transfer into the interior of the particle, characterized by an intraparticle diffusion coefficient, can be the slowest step. The most commonly used is IPD model of Weber and Morris. The IPD model for 4-CP on AF5 with S1 and S2 was shown on Fig. 6. The slope of the plots gave the value of k_i (Table 3). The plots are not linear over the whole time range, indicating that more than one step is involved in the sorption of 4-CP on AF5 with S1 and S2. The intraparticle diffusion kinetic plot in fragmented form showed two types of linearity indicating two diffusion stages of 4-CP

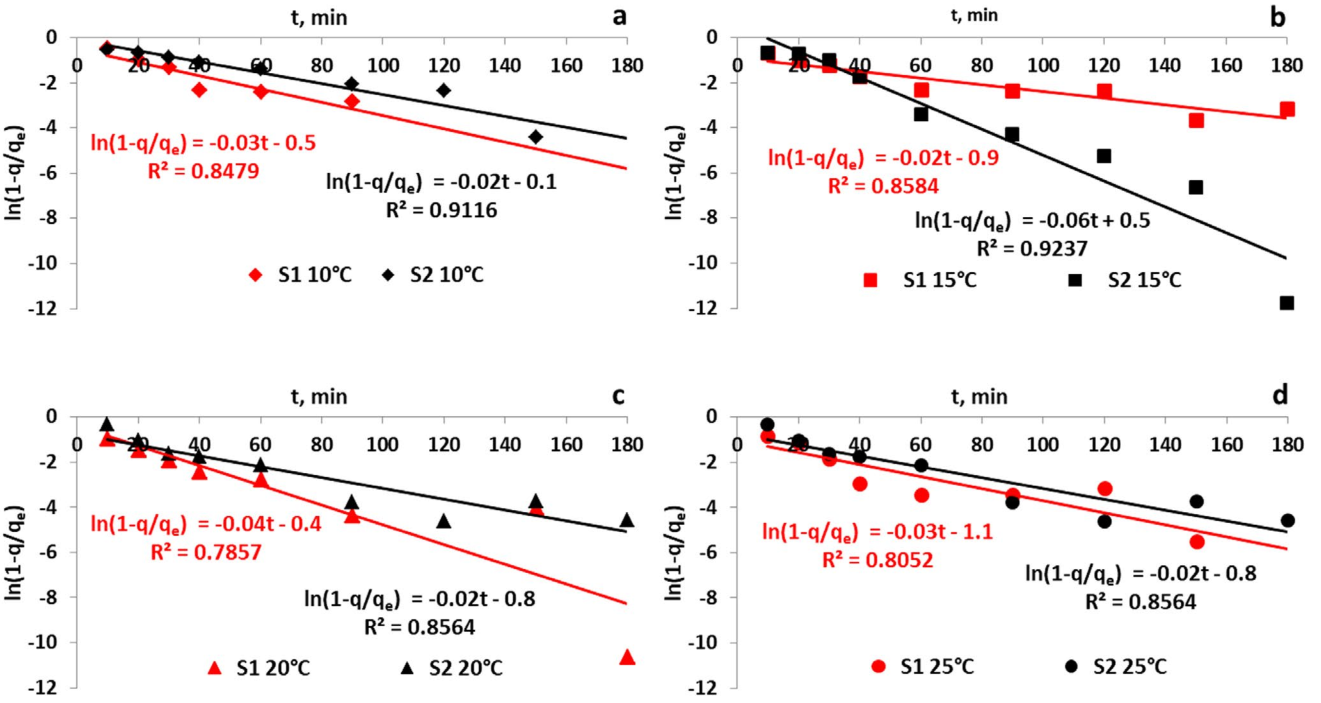

Fig. 5. Liquid film diffusion kinetic plot for 4-CP sorption on AF5 with S1 and S2 solutions: (a) 10°C, (b) 15°C, (c) 20°C, and (d) 25°C.

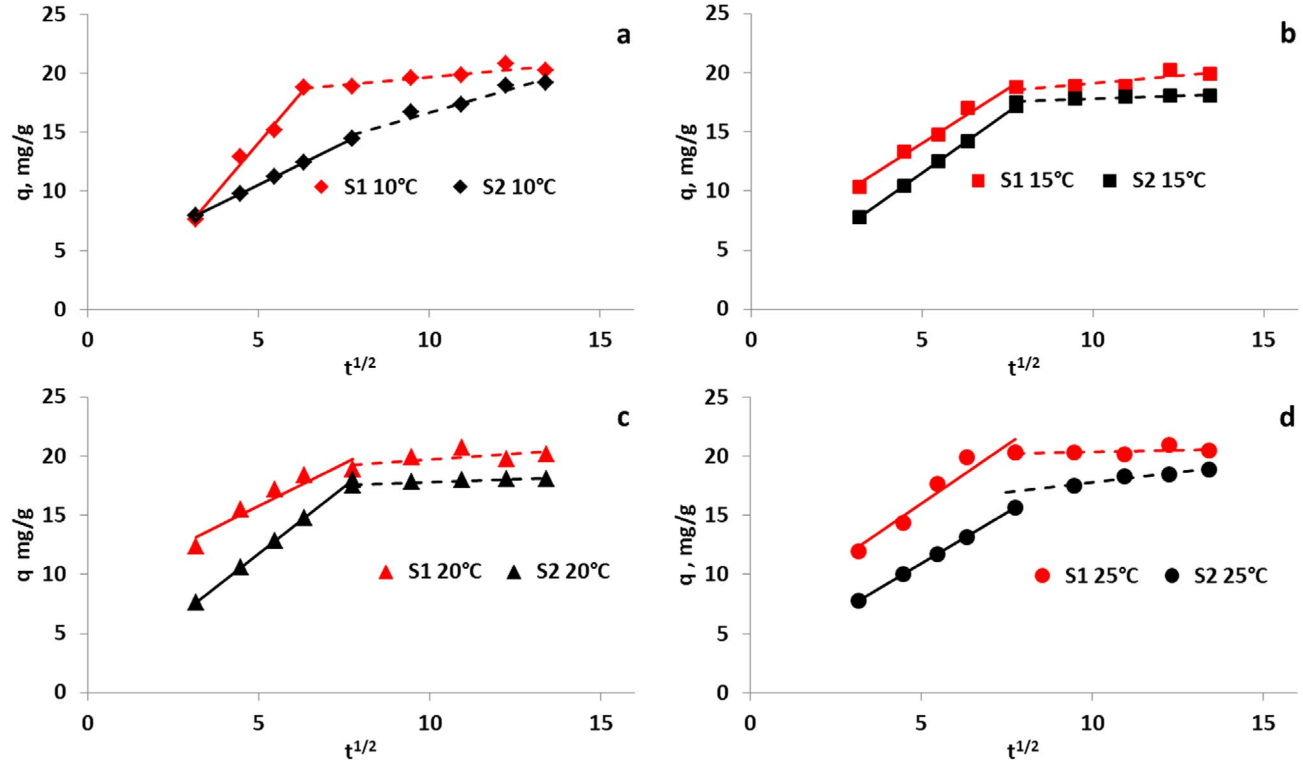

Fig. 6. Intraparticle diffusion kinetic plot for 4-CP sorption onto AF5 with S1 and S2 in fragmented form: (a) 10°C, (b) 15°C, (c) 20°C, and (d) 25°C.

Table 3
Kinetic parameters of IPD model for 4-CP sorption with S1 and S2 on AF5

	k_{i1}, mg/g min$^{1/2}$	c_1, mg/g	R^2	Δq	k_{i2}, mg/g min$^{1/2}$	c_2, mg/g	R^2	Δq
Temperature	S1							
10°C	2.54	0.89	0.9049	0.100	0.28	16.81	0.7875	0.016
15°C	1.85	4.79	0.9858	0.026	0.26	16.56	0.6644	0.023
20°C	1.90	6.61	0.9867	0.020	0.19	17.85	0.4002	0.025
25°C	2.56	3.54	0.9846	0.031	0.06	19.77	0.2032	0.013
Temperature	S2							
10°C	1.41	3.50	0.9819	0.036	10.07	0.9692	0.9394	0.125
15°C	2.05	1.28	0.9375	0.092	17.27	0.9572	0.9162	0.478
20°C	2.26	0.47	0.8164	0.228	17.75	0.3825	0.1463	0.573
25°C	1.71	2.35	0.8834	0.760	14.37	0.9633	0.9280	0.264

adsorption onto AF5. In both S1 and S2, at all temperatures tested first stage plot passed near the origin whereas the second one did not. It was concluded that the second stage was controlled by both film and intraparticle diffusions. Both in the case of 4-CP sorption from single-component S1 and S2 containing lead(II) ions at all temperatures tested the $k_{i1} > k_{i2}$ was attributed to the faster rate of film diffusion than intraparticle diffusion. It was concluded that the sorption kinetics might be controlled by film diffusion and intraparticle diffusion simultaneously.

4. Conclusion

The presence of lead(II) affects 4-CP sorption on AF5 synthetic activated carbon. The dynamic equilibrium state of sorption in a two-component (S2) solution containing 4-CP and Pb(II) 4-CP is established for a longer time than in a one-component solution (S1) containing only an organic compound. The removal efficiency of 4-CP on AF5 is high (80.4%–86.8%), and the presence of lead(II) in the solution reduces it by several percentage.

4-CP sorption in the presence of lead(II) and in the absence of this component follows the PSO model, suggesting the chemical nature of the process. In both research systems, the value of the constant k_2 of the PSO model does not depend on temperature. Activation energy values for 4-CP sorption on AF5 are 45.3 and 28.8 kJ/mol for S1 and S2, respectively, and correspond to the chemical sorption activation energy. The approaching equilibrium parameter based on Elovich equation (R_E) analysis confirms the chemical nature of the process as well as the fact that sorption in 4-CP in the presence of lead(II) occurs more slowly. The approaching equilibrium factor (R_w) analysis in the PSO model indicates that in the presence of lead(II), the conditions for achieving 4-CP sorption equilibrium deteriorate.

The speed of the 4-CP sorption process on AF5 activated carbon without and in the presence of lead(II) is influenced by diffusion through the boundary layer and intraparticle diffusion.

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Symbols

4-CP — 4-Chlophenol
A — Temperature independent factor
AF5 — Synthetic activated carbon
a — Constant of Elovich model, the initial sorption rate
b — Constant of Elovich model, the desorption constant
C_e — Equilibrium concentration of 4-CP
C_0 — Initial concentration of 4-CP
C_t — Equilibrium concentration of 4-CP at time t
c — Constant of IPD model
E — Elovich model
E_a — Activation energy of adsorption
F — Fractional attainment of equilibrium
h — Initial sorption rate
IPD — Intraparticle diffusion
k_1 — Rate constant of PFO model
k_2 — Rate constant of PSO model
k_{fd} — Film diffusion rate constant
k_i — Intraparticle diffusion rate constant
LFM — Liquid film diffusion model
m — Mass
N — Number of data points
pK_a — Logarithmic acid dissociation constant
PFO — Pseudo-first order kinetic model
PSO — Pseudo-second order kinetic model
q — Sorption capacity in time
q_{cal} — Calculated sorption capacity
q_e — Amount of sorption at equilibrium
q_{exp} — Experimental sorption capacity
R — Ideal gas constant
RE — Removal efficiency of 4-CP
R^2 — Coefficient of determination

R_E — Approaching equilibrium parameter based on Elovich equation
R_i — Initial factor based on IPD model
R_w — Approaching equilibrium factor in the PSO model
S1 — Solution of 4-CP
S2 — Solution of 4-CP and Pb(II)
SD — Standard deviation
T — Solution temperature
TOC — Total organic carbon
t — Time
V — Volume of sample

References

[1] U. Dmitruk, E. Zbieć, J. Dojlido, Chlorophenols in water environment, Och. Sr., 28 (2006) 25–28.

[2] J. Michałowicz, The occurrence of chlorophenols, chlorocatechols and chlorinated methoxyphenols in drinking water of the largest cities in Poland, Pol. J. Environ. Stud., 14 (2005) 327–333.

[3] T. Ge, J. Han, Y. Qi, X. Gu, L. Ma, Ch. Zhang, S. Naeem, D. Huang, The toxic effects of chlorophenols and associated mechanisms in fish, Aquat. Toxicol., 184 (2017) 78–93.

[4] 2455/2001/EC. Decision No 2455/2001/EC of the European Parliament and the Council of November 20, 2001 Establishing the List of Priority Substances in the Field of Water Policy and Amending Directive 2000/60/EC.

[5] L. Dąbek, E. Ozimina, A. Picheta-Oleoeś, Applying the combined processes of sorption and oxidation to remove organic compounds from an aqueous environment using the example of p-chlorophenol, Ecol. Chem. Eng. A, 19 (2012) 275–286.

[6] P. Bhatt, M.S. Kumar, S. Mudliar, T. Chakrabarti, Biodegradation of chlorinated compounds – a review, Crit. Rev. Environ. Sci. Technol., 37 (2007) 165–198.

[7] Q.-S. Liu, T. Zheng, P. Wang, J.-P. Jiang, N. Li, Adsorption isotherm, kinetic and mechanism studies of some substituted phenols on activated carbon fibers, Chem. Eng. J., 157 (2010) 348–356.

[8] R.-L. Tseng, K.-T. Wu, F.-Ch Wu, R.-S. Juang, Kinetic studies on the adsorption of phenol, 4-chlorophenol and 2,4-dichlorophenol from water using activated carbons, J. Environ. Manage., 91 (2010) 2208–2214.

[9] Y. Omidi-Khaniabadi, A. Jafari, H. Nourmoradi, F. Taheri, S. Saeedi, Adsorption of 4-chlorofenol from aqueous solution using activated carbon synthesized from aloe vera green wastes, JAEHR, 3/2 (2015) 120–129.

[10] S. Madannejad, A. Rashidi, S. Sadeghhassani, F. Shemirani, E. Ghasemy, Removal of 4-chlorophenol from water using different carbon nanostructures: a comparison study, J. Mol. Liq., 249 (2018) 877–885.

[11] K. Kuśmierek, L. Dąbek, W. Kamiński, A. Świątkowski, Evaluation of the usefulness of peat for removal of chlorophenols from water solutions, Ochr. Sr., 35 (2013) 51–55.

[12] Q. Qin, K. Liu, D. Fu, H. Gao, Effect of chlorine content of chlorophenols on their adsorption by mesoporous SBA-15, J. Environ. Sci., 24 (2012) 1411–1417.

[13] S. Manahan, Environmental Toxicology. Chemical and Biochemical Aspects, Wydawnictwo Naukowe PWN, Warszawa, 2006.

[14] Regulation of the Minister of the Environment of November 18, 2014, on the conditions to be met when discharging sewage into water or into the ground, and on substances that are particularly harmful to the aquatic environment (Dz.U.2014, poz.1800).

[15] J. Nawrocki (red.), Water Treatment. Physical, Chemical and Biological Processes Wydawnictwo Naukowe UAM, Wydawnictwo Naukowe PWN, Warszawa, 2010.

[16] L. Reczek, M.M. Michel, T. Siwiec, E. Żukowska, Sorption of Pb(II) ions onto some filter materials used in water treatment technology, Przem. Chem., 93/11 (2014) 1978–1982.

[17] L. Largiette, P. Lodewyckx, Studying different methods to determine the thermos kinetic constants in the adsorption of Pb^{2+} on an activated carbon from Bois carré seeds, J. Environ. Chem. Eng., 2 (2014) 788–795.

[18] L. Largitte, J. Laminie, Modelling the lead concentration decay in the adsorption of lead onto a granular activated carbon, J. Environ. Chem. Eng., 3 (2015) 474–481.

[19] L. Largitte, R. Pasquier, A review of the kinetics adsorption model and their application to the adsorption of lead by an activated carbon, Chem. Eng. Res. Des., 109 (2016) 495–504.

[20] L. Reczek, M.M. Michel, K. Kuśmierek, A. Świątkowski, T. Siwiec, Sorption of 4-chlorophenol and lead on granular activated carbon: equilibrium, kinetics and thermodynamic, Desal. Wat. Treat., 62 (2017) 369–376.

[21] M. Irani, M. Amjadi, M.A. Mousavian, Comparative study of lead sorption onto natural perlite, dolomite and diatomite, Chem. Eng. J., 178 (2011) 317–323.

[22] M. Sprynskyy, B. Buszewski, A. Terzyk, J. Namieśnik, Study of the selection mechanism of heavy metal (Pb^{2+},Cu^{2+} and Cd^{2+}) adsorption on clinoptilite, J. Colloid Interface Sci., 304 (2006) 21–28.

[23] B.C. Qi, C. Aldrich, Biosorption of heavy metals from aqueous solutions with tobacco dust, Bioresour. Technol., 91 (2008) 2321–2329.

[24] A. Witek-Krowiak, R. Szafran, Sz. Modelski, Biosorption of heavy metals from aqueous solutions onto peanut shell as a low-cost biosorbent, Desalination, 265 (2011) 126–134.

[25] S. Andini, R. Cioffi, F. Montagnaro, F. Pisciotta, L. Santoro, Simultaneous adsorption of chlorophenol and heavy metal ions on organophilic bentonite, Appl. Clay Sci., 31 (2006) 126–133.

[26] Z.-g Pei, X.-q. Shan, T. Liu, Y.-n. Xie, B. Wen, S. Zhang, S.U. Khan, Effect of lead on the sorption of 2,4,6-trichlophenol on soil and peat, Environ. Pollut., 147 (2007) 764–770.

[27] H. Yang, Y. Hu, H. Cheng, Sorption of chlorophenols on microporous minerals: mechanism and influence of metal cations, solution pH, and humic acid, Environ. Sci. Pollut. Res., 23 (2016) 19266–19280.

[28] L. Reczek, Models Describing Lead(II) Sorption Kinetics on Synthetic Carbon Material, Wydawnictwo SGGW, Warsaw, 2019.

[29] S. Lagergren, Zur theorie der Sogenannten adsorption gelöster stoffe, K. Sven. Vetenskapsakad. Handl., 24 (1898) 1–39.

[30] Y.S. Ho, Second order kinetic model for the sorption of cadmium onto tree fern: a comparison of linear and nonlinear methods, Water Res., 40 (2006) 119–125.

[31] S.Y. Elovich, O.G. Larinov, Theory of adsorption from solutions of non-electrolytes on solid (I) equation adsorption from solutions and the analysis of its simplest form, (II)verification of the equation of adsorption isotherm from solutions, Izv. Akad. Nauk. SSSR, Otd. Khim. Nauk, 2 (1962) 209–216.

[32] H.N. Tran, S.-J. You, A. Hosseini-Bandegharaei, H.-P. Chao, Mistakes and inconsistencies regarding adsorption of contaminants from aqueous solutions: a critical review, Water Res., 120 (2017) 88–116.

[33] G.E. Boyd, A.M. Adamson, L.S. Myers, The exchange adsorption of ions from aqueous solutions by organic zeolites. II Kinetics, J. Am. Chem. Soc., 69 (1947) 2836–2848.

[34] W.J. Weber, J. Morris, Kinetics of adsorption on carbon from solution, J. Sanit. Eng. Div., 89 (1963) 31–59.

[35] H. Ding, X. Li, J. Wang, X. Zhang, CH. Chen, Adsorption of chlorophenols from aqueous solutions by pristine and surface functionalized single-walled carbon nanotubes, J. Environ. Sci., 43 (2016) 187–198.

[36] C. Moreno-Castilla, Adsorption of organic molecules from aqueous solutions on carbon materials, Carbon, 42 (2004) 83–94.

[37] R.C. Bansal, M. Goyal, Activated Carbon Adsorption, CRC Press, Taylor & Francis Group, Boca Raton, 2005.

[38] Y.S. Ho, G. McKay, Pseudo-second order model for sorption process, Process Biochem., 34 (1999) 451–465.

[39] B.H. Hameed, L.H. Chin, S. Rengaraj, Adsorption of 4-chlorofenol onto activated carbon prepared from rattan sawdust Desalination, 225 (2008) 185–198.

[40] K. Kuśmierek, A. Świątkowski, The influence of an electrolyte on the adsorption of 4-chlorofenol onto activated carbon and multi-walled carbon nanotubes, Desal. Wat. Treat., 56 (2015) 2807–2816.

[41] H.N. Tran, S.-J. You, H.-P. Chao, Thermodynamic parameter of cadmium adsorption onto orange peel calculated from various methods: a comparison study, J. Environ. Chem. Eng., 4 (2016) 2671–2682.

[42] Z. Aksu, E. Kabasakal, Batch adsorption of 2,4-dichlorophenoxy-acetic acid (2,4D) from aqueous solution by granular activated carbon, Sep. Purif. Technol., 35 (2004) 223–240.

[43] A.M. Soliman, H.M. Elwy, T. Thiemann, Y. Majedi, F.T. Labata, A.F. Al-Rawashed, Removal of Pb(II) ions from aqueous solutions by sulphuric acid-treated palm tree leaves, J. Taiwan Inst. Chem. Eng., 58 (2016) 264–273.

[44] F.C. Wu, R.L. Tseng, S.C. Hung, R.S. Juang, Characteristics of pseudo-second-order kinetic model for liquid-phase adsorption: a mini-review, Chem. Eng. J., 151 (2009) 1–9.

[45] F.C. Wu, R.L. Tseng, R.S. Juang, Characteristics of Elovich equation used for the analysis of adsorption kinetics in dye-chitosan systems, Chem. Eng. J., 150 (2009) 366–373.

[46] S.S. Gupta, K.G. Bhattacharyya, Adsorption of Ni(II) on clays, J. Colloid Interface Sci., 295 (2006) 21–32.