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NUMERICAL MODELING OF KINETICS OF HEAVY METAL SORPTION FROM POLLUTED WATER

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Abstract. Water protection is one of the most important priorities of environmental protection. It is necessary to reduce pollution of wastewater in order to reduce pollution of drinking-water and water pools. One of the most dangerous wastewater pollutants are heavy metals (HM). They have a negative influence on people and aquatic water systems. The paper analyses possibilities of the sorption method application for heavy metal elimination from wastewater. Experimental investigation of HM sorption from water and numerical modeling usage possibilities for prognosis of the HM sorption kinetic process was carried out as well as experimental study of HM elimination efficiency dependence on sorption time of HM from wastewater, when using sorbents. Two pseudo kinetic models, i e the pseudo first- and second-order models, were developed on the basis of experimental investigation. These models were applied in numerical modeling in the computer program PHOENICS. The results of the computer program PHOENICS and those of experimental investigation describing HM sorption from water were compared. After comparing the two pseudo models, it is determined that the pseudo second-order model suits better for HM sorption.

Keywords: sorption, sorbents, heavy metals (HM), pseudo kinetic models, numerical modeling.

1. Introduction

Heavy metals (HM) are very hazardous substances having a long-lasting impact on ecosystems [1]. They have a complex negative impact on human health, animals, flora and fauna in water sources and micro flora of wastewater [2]. Commonly, the concentration of HM exceeds a maximal available concentration in water (wastewater) and in the soil [3]. HM enter ecosystems in their wet and dry forms from local or outer atmosphere sources; they are also washed from putrid or putrescent plants that concentrate in the soil or they are brought by wind or water together with mineral particles [4–7].

Pollutants emitted to the environment or water can be eliminated bu using synthetic or natural materials, for example, tobermorite mineral can be used in the environment protection area and building industry [8]. For our investigation we selected lead (Pb) as the most common HM. Natural and synthetic sorbents for their high sorption capacity, selectivity, properties of cation exchangeability, a low price and affordability were used to remove HM from wastewater [9]. Experimental investigation of HM elimination efficiency dependence on sorption time for wastewater, when using sorbents, was carried out. Investigation methodology is described in literature [10]. Mathematical modeling is used to describe the processes and phenomena in different systems (technical, physical, ecological, economic, etc) because a scientific and natural experiment is either long or dangerous, either simply impossible because most of these systems are unique. The price of errors in handling these processes and phenomena is extremely high. The essence of mathematical modeling is based on substitution of an initial object of modeling (events, processes, phenomena) by its "image", i e mathematical model, and future study of this model by means of known mathematical methods.

There are some programs, like FLUENT, PHOENICS, etc that can be applied in order to simulate numerically the variation of metal concentration in a liquid phase during the sorption process from an aqueous solution.

FLUENT is the world's largest provider of computational fluid dynamics (CFD) software and consulting services. Our software is used for simulation, visualization and analysis of fluid flow, heat and mass transfer and chemical reactions [11].

In our case we choose the program PHOENICS 1.4 version because it is more suitable and much easier in introduction of required data and application in numerical modeling the variation of heavy metal concentration in a

liquid phase during the sorption of metals from polluted water.

PHOENICS is used by environmental specialists for the prediction and possible control of an environmental impact and hazards. PHOENICS embodies the techniques of Computational Fluid Dynamics (CFD). CFD is a computer-based methodology for the solution of the fundamental equations of fluid flow.

Numerical modeling was performed for polluted water for calculating the sorption capacity of a sorbent during a different sorption time. A numerical model of the sorption process was created sustaining the results of theoretical calculations. Empirical formulas that were calculated by the smallest square method were introduced into the program PHOENICS to determine dependence of the sorption capacity of a sorbent on a different time of sorption (after 5–720 min from the beginning of sorption) by the results obtained during theoretic calculations. These empirical formulas depict the sorption capacity of sorbent KU–2–8 depending on the terms of sorption. Empirical equations with ingoing values of coefficients (the ratio constant of pseudo second-order kinetic model $k_{1,ad}$, the ratio constant of pseudo second-order kinetic model $k_{2,ad}$, initial sorption rate h and sorption capacity at equilibrium q_{eq}) were introduced into the program.

2. The purpose of the work

The main purpose of this study was theoretical calculating of the sorption capacity of a sorbent during water purification from Pb on cation-exchange resin KU. Pseudo first- and second-order kinetic models were applied for description of Pb sorption kinetics.

3. Description of theoretical investigation

Numerical modeling was carried out during the work with application of differential equations of the transfer processes of the variation of sorbent sorption capacity, depending on the period of sorption in the system cation-exchange resin KU–2–8/Pb aqueous solution [12–14]. Experimental investigation of Pb sorption from polluted water was performed, and theoretical models were created. The data received during experimental investigation were compared with those of the theoretical model, and a theoretical model, that has the best conformity with the experiment, was chosen.

4. Area of modeling

Sorption takes place in the system cation-exchange resin KU–2–8/Pb aqueous solution. The field of calculation was composed of 4 gratings in axial X direction. While solving the task, the following parameters were set: sorbent sorption capacity corresponding to the coefficients that were mentioned above – the ratio constant of the pseudo first- order kinetic model $k_{1,ad}$, the ratio constant of the pseudo second-order kinetic model $k_{2,ad}$, initial sorption rate h and sorption capacity at equilibrium q_{eq}. Sorbent sorption capacities were calculated, while solving the task. It was simulated how the sorption capacity of sorbent KU–2-8, changes, depending on a different sorption time. Empirical pseudo first- and second- order formulas describing variation of Pb sorption capacity, depending on sorption time, were introduced for each Pb concentration. These formulas were calculated by the method of the smallest square trying to express dependence between sorbent sorption capacity and time (in axial X direction) by an empirical formula the correlation coefficient of which would be closer to the unit, so that it would match as precisely as possible the theoretical data. With the help of the program PHOENICS, sorbent sorption capacity in the system sorbent/Pb aqueous solution was calculated after 5–720 min from the beginning of sorption, while the initial concentrations of Pb in water were: C_{Pb1} = 2 mg/l, C_{Pb2} = 10 mg/l, C_{Pb3} = 100 mg/l, C_{Pb4} = 1000 mg/l, C_{Pb5} = 4000 mg/l. The time step is 5 min. Pb concentration in the solution remaining after 1440 min from the beginning of sorption was chosen as an equilibrium sorption capacity q_{eq}.

5. Method of solution

After a particular sorption time the empirical formulas applying TREND function of EXCEL program were introduced into the PHOENICS program with PLANT in order to calculate sorption capacity. Pseudo first- and second-order empirical models, describing sorbent sorption capacity, depending on the time of sorption, were chosen. These formulas were calculated by the method of the smallest square trying to express dependence of sorbent sorption capacity on the sorption time (in axial X direction) by an empirical formula that would have the correlation coefficient nearest to the unit, so that the formula would match as precisely as possible the results obtained by theoretical calculations. Sorbent sorption capacity was obtained, while solving transfer equations, and thereby particular sorption time, corresponding to sorbent sorption capacity depending on time, was calculated (in the direction of X axial coordinate).

6. Results of modeling

Experimental investigation of the sorption of Pb ions from aqueous solutions onto cation-exchange resin KU–2-8 was performed for a different sorption time (5 min, 30 min, 60 min 720 min. and 1440 min) at 5 different concentrations of Pb in water (2 mg/l, 10 mg/l, 100 mg/l, 1000 mg/l and 4000 mg/l). The ratio of a sorbent with the solution was 1:100. 0,5 g of a sorbent was poured with 50 ml of the investigated solution. After each period of time the samples of Pb -polluted water were analysed with an atomic absorption spectrophotometer. By the obtained retained metal concentration in the solution, sorption capacities for Pb were calculated at each time point and for each metal concentration studied during the investigation. Sorption capacities of Pb are shown in Table 1.

As we can notice from Table 1, sorption capacity for Pb increases with increasing time of sorption. The figures show that the sorption capacities of Pb increased with initial metal concentration in solutions as well. At each of the 5 initial concentrations after 1440 minutes from the beginning of its sorption equilibrium was set. Several models can be used to express the mechanism of solute sorption onto a sorbent. In order to analyse the sorption kinetics of Pb the pseudo first-order and second-order kinetic models were applied to the experimental data.

The pseudo first-order rate expression of Lagergren can be expressed as

$$\log(q_{eq} - q_t) = \log q_{eq} - k_{1,ad} t\,, \qquad (1)$$

where q_{eq} – sorption capacity at equilibrium, mg/g; q_t – sorption capacity at time t, mg/g; $k_{1,ad}$ – the rate constant of pseudo first-order sorption, min^{-1}.

If equation (1) is applicable, the sorption rate is the pseudo first-order reaction, and the rate constant $k_{1,ad}$ can be obtained from the slope of the plot of $\log(q_{eq} - q_t)$ against t. The pseudo second-order rate equation can be expressed as

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_{eq}} t\,, \qquad (2)$$

where $h = k_{2,ad} q_e^2$ – initial sorption rate, mg pollutant/g sorbent min; $k_{2,ad}$ – rate constant of pseudo second-order kinetic model, g sorbent/mg pollutant min.

If equation (2) is applicable, the plot of t/q_t against t should give a linear relationship, and q_{eq} and $k_{2,ad}$ can be determined from the slope and intercept of the plot, and there is no need to know any parameter beforehand. The pseudo second-order equation is based on the sorption capacity in a solid phase [15]. An average percentage difference between the measured and calculated sorption capacities is calculated by the following equation [16]:

$$\text{Erorr}(\%) = \frac{100}{N} \sum_{k=1}^{N} \left[\frac{|q_{\exp} - q_{cal}|}{q_{\exp}} \right], \qquad (3)$$

where $q_{\exp}$ – experimental sorption capacity, mg/g; q_{cal} – calculated sorption capacity, mg/g; N – number of experiments.

The values of model parameters $k_{1,\,ad}$, $k_{2,\,ad}$, q_{eq}, correlation coefficients R^2 and average percentage difference between the measured and calculated sorption capacities are obtained and presented in Table 2.

Table 1. Calculated sorption capacities for Pb

Time, min	Sorption capacity a, mg/g				
	2 mg/l	10 mg/l	100 mg/l	1000 mg/l	4000 mg/l
5	0,009	0,262	2,000	16,306	26,144
30	0,022	0,434	2,615	21,844	30,760
60	0,040	0,586	2,751	26,251	39,513
720	0,098	0,757	3,051	32,658	53,412

The main results of the sorption capacity of cation-exchange resin KU–2-8, obtained when the concentration of Pb was 2 mg/l, 10 mg/l, 100 mg/l, 1000 mg/l and 4000 mg/l during numerical modeling when pseudo second-order empirical formulas were applied, are shown in Figs 1–5. Empirical formulas (4–8) for the pseudo first-order model were introduced into the program PHOENICS when: C(Pb) = 2 mg/l (4), C(Pb) = 10 mg/l (5), C(Pb) = 100 mg/l (6), C(Pb) = 1000 mg/l (7), C(Pb) = 4000 mg/l (8). Empirical formulas (9–13) for the pseudo second-order model were introduced into the program PHOENIC when: C(Pb) = 2 mg/l (9), C(Pb) = 10 mg/l (10), C(Pb) = 100 mg/l (11), C(Pb) = 1000 mg/l (12), C(Pb) = 4000 mg/l (13).

$$y = -0{,}0005x - 0{,}8407; \qquad (4)$$

$$y = -0{,}0007x - 0{,}3146; \qquad (5)$$

$$y = -0{,}0005x + 0{,}0094; \qquad (6)$$

$$y = -0{,}0004x + 1{,}3558; \qquad (7)$$

$$y = 9{,}0643x + 864{,}0100; \qquad (8)$$

$$y = x/(9{,}0643x + 864{,}01); \qquad (9)$$

$$y = x/(1{,}2896x + 22{,}537); \qquad (10)$$

$$y = x/(0{,}3256x + 1{,}599); \qquad (11)$$

$$y = x/(0{,}0301x + 0{,}3635); \qquad (12)$$

$$y = x/(0{,}0183x + 0{,}3111). \qquad (13)$$

As shown in Table 2, the correlation coefficient for the second-order rate equation is greater than 0,9 and sub-

Table 2. Comparison of the first-order and second-order rate constants for different initial metal concentration

Initial Pb concentration, mg/l	First-order kinetic model				$q_{eq,\exp}$, mg/g
	$K_{1,\,ad}$ $\times 10^{-2}$, (g mg_{-1} min^{-1})	q_{eq}, mg/g	R^2	$Error_2$, %	
2	–0,05	0,14	0,908	11,51	0,16
10	–0,07	0,48	0,867	46,25	0,90
100	–0,05	1,02	0,709	70,61	3,48
1000	–0,04	22,69	0,861	48,07	43,69
4000	–0,08	30,75	0,853	50,03	61,53
Average	–	–	–	45,29	–
	Second-order kinetic model				
Initial Pb concentration, mg/l	$K_{2,\,ad}$ $\times 10^{-2}$, (g mg_{-1} min^{-1})	q_{eq}, mg/g	R^2	$Error_2$, %	$q_{eq,\exp}$, mg/g
2	9,71	0,11	0,874	32,35	0,16
10	7,38	0,78	0.901	13,99	0,90
100	6,63	3,07	0,906	11,66	3,48
1000	0,25	33,22	0,889	23,96	43,69
4000	0,11	54,64	0,909	11,19	61,53
Average	–	–	–	18,63	–

stantially higher than for the first-order rate equation. Also, the q_{eq} values calculated from the second-order kinetic model correspond well with the experimental values. An average percentage difference between the measured and calculated sorption capacities (Table 2) for the pseudo first-order model (error = 45,29 %) is particularly greater than the error value for the second-order kinetic model (error = 18,63 %). Dependence of Pb sorption capacity (*a*, mg/g) on time (*t*, min) calculated by using the pseudo second--order model, is presented in Figs 1–5.

This shows that the agreement of the experimental data and the pseudo second-order equation is much better than for the first-order equation. The sorption of Pb onto cation-exchange resin was plotted with an excellent extremely high correlation coefficient 0,9. This shows that the sorption of Pb can be represented by a pseudo second-order reaction.

We can see linear dependence of Pb sorption capacity (*a*, mg/g) on time (*t*, min) calculated with the help of pseudo second-order model in Fig 1. Sorption capacity of a sorbent increased from 0,005 to 0,097 mg/g in the system cation-exchange resin KU-2-8/ Pb aqueous solution. We can also see linear dependence of Pb sorption capacity (*a*, mg/g) on time (*t*, min) calculated with the help

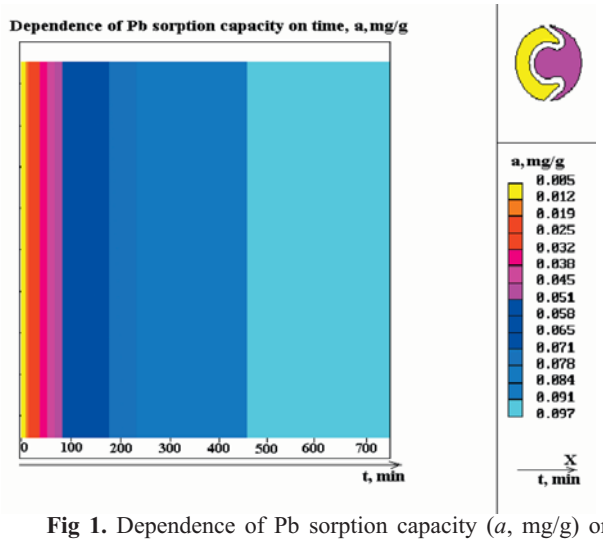

Fig 1. Dependence of Pb sorption capacity (*a*, mg/g) on time (*t*, min) calculated using pseudo second-order model (experimental conditions): *T* = 20 °C; ratio mass of sorbent: mass of solution =1:100, C(Pb) = 2 mg/l), modeling conditions: *t* = 0–720 min; time step = 5 min

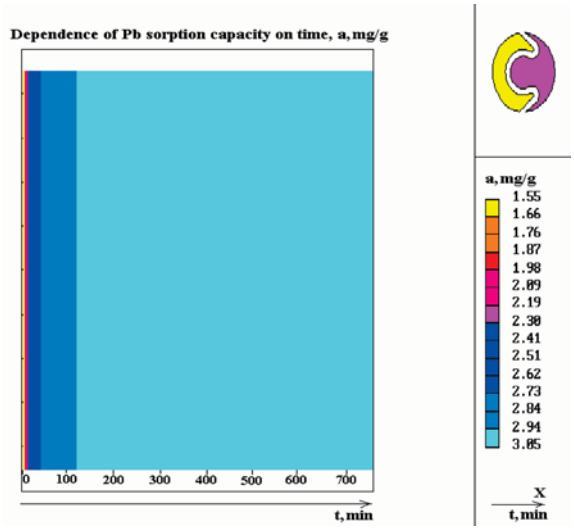

Fig 3. Dependence of Pb sorption capacity (*a*, mg/g) on time (*t*, min) calculated using pseudo second-order model (experimental conditions): *T* = 20 °C; ratio mass of sorbent: mass of solution =1:100, C(Pb) = 100 mg/l), modeling conditions: *t* = 0–720 min; time step = 5 min

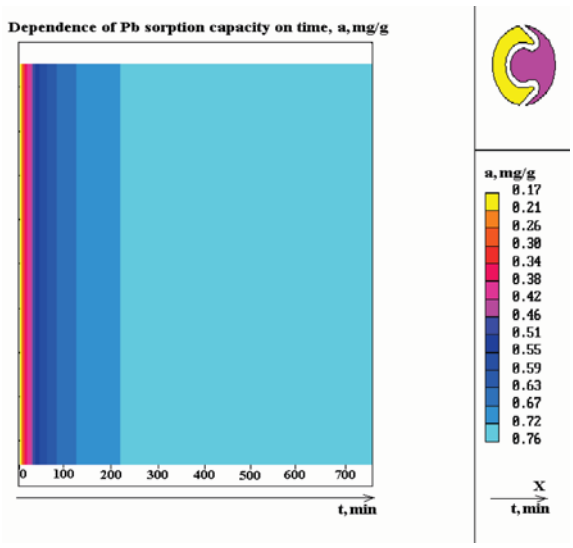

Fig 2. Dependence of Pb sorption capacity (*a*, mg/g) on time (*t*, min) calculated using pseudo second-order model (experimental conditions): *T* = 20 °C; ratio mass of sorbent: mass of solution =1:100, C(Pb) = 10 mg/l), modeling conditions: *t* = 0–720 min; time step = 5 min

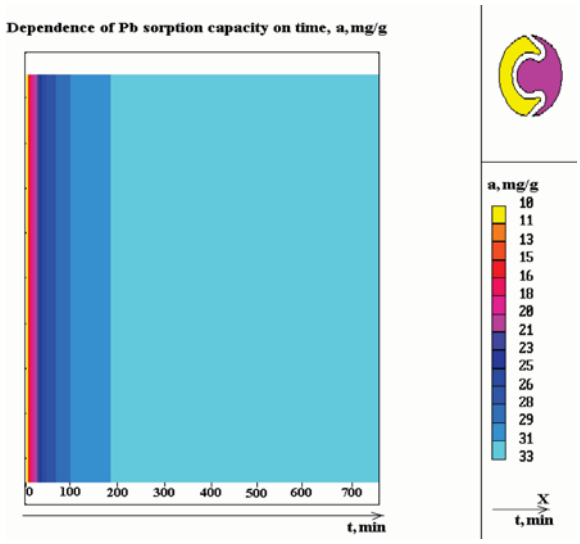

Fig 4. Dependence of Pb sorption capacity (*a*, mg/g) on time (*t*, min) calculated using pseudo second-order model (experimental conditions): *T* = 20 °C; ratio mass of sorbent: mass of solution =1:100, C(Pb) = 1000 mg/l), modeling conditions: *t* = 0–720 min; time step = 5 min

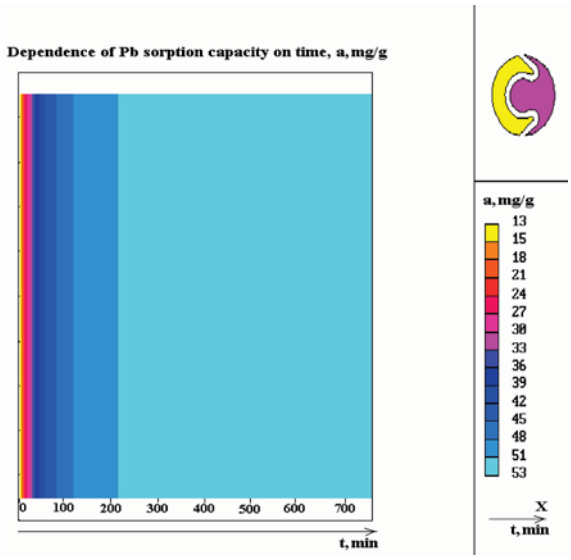

Fig 5. Dependence of Pb sorption capacity (*a*, mg/g) on time (*t*, min) calculated using pseudo second-order model (experimental conditions): T = 20 ºC; ratio mass of sorbent: mass of solution =1:100, C(Pb) = 4000 mg/l), modeling conditions: t = 0–720 min; time step = 5 min

of pseudo second-order model in Fig 2. The sorption capacity of a sorbent increased from 0,17 to 0,76 mg/g in the system cation-exchange resin KU–2-8/ Pb aqueous solution. In this case increase of sorption capacity is more rapid than in Fig 1. The reason of this process can be a bigger concentration of Pb in an aqueous solution (10 mg/l instead of 2 mg/l).

Linear dependence of Pb sorption capacity (*a*, mg/g) on time (*t*, min) calculated with the help of the pseudo second-order model is also observed in Fig 3. The sorption capacity of a sorbent increased from 1,55 to 3,05 mg/g in the system cation-exchange resin KU–2-8/ Pb aqueous solution. In this case increase of sorption capacity is more rapid than in Figs 1 and 2. The reason of this process can be a bigger concentration of Pb in an aqueous solution (100 mg/l instead of 10 mg/l or 2 mg/l).

The sorption capacity of a sorbent increased from 10 to 33 mg/g in the system cation-exchange resin KU–2-8/ Pb aqueous solution. In this case increase of sorption capacity is more rapid than in Figs 1–3. The reason of this process can be a bigger concentration of Pb in an aqueous solution (1000 mg/l instead of 100 mg/l, 10 mg/l or 2 mg/l). We can see that the results of a physical experiment are similar to modeling results. The sorption capacity of a sorbent increased from 13 to 53 mg/g in the system cation-exchange resin KU–2-8/ Pb aqueous solution. Numerical modeling and programme PHOENICS can be used for calculating Pb sorption capacity (*a*, mg/g) on time (*t*, min). Sorption kinetics of Pb was calculated using pseudo models, i e the pseudo first- and second-order models. The results of numerical modeling show that numerical modeling can change a physical experiment. The results presented in Tables 1, 2 and in Figs 1–5 show that the pseudo second-order model is more adequate to a physical experiment than the pseudo first-order model.

7. Conclusions

1. A numerical model of the sorption process, allowing to forecast the sorption capacity of sorbent KU–2-8, depending on the time of the sorption process, was set using the program PHOENICS 1.4 version.

2. Pseudo first- and second-order kinetic models were applied in order to characterize the sorption capacity of a sorbent in the system cation-exchange resin KU–2-8/Pb aqueous solution.

3. The uptake capacity of sorbent sorption increases with increase of initial metal concentration. Also, uptake capacity increases with increasing time of sorption. When t = 1440 min of sorption, sorption capacity equilibrium is reached.

4. The results of the investigation show that the agreement of the experimental data and the pseudo second-order kinetic model is much better than the data of the pseudo first-order kinetic model. The sorption of Pb onto cation-exchange resin KU–2-8 was plotted with an excellent correlation coefficient R^2 = 0,9, and an average error for the second-order model was 18,63 %.

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SKAITINIS SUNKIŲJŲ METALŲ SORBCIJOS IŠ UŽTERŠTO VANDENS KINETIKOS MODELIAVIMAS

D. Paliulis

S a n t r a u k a

Vandens apsauga yra vienas iš svarbiausių aplinkos apsaugos prioritetų. Norint sumažinti vandens telkinių ir geriamojo vandens taršą, būtina mažinti išleidžiamų nuotekų užterštumą. Vieni iš pavojingiausių nuotekų teršalų – sunkieji metalai, galintys sukelti neigiamą poveikį žmonėms bei vandens ekosistemoms.

Straipsnyje nagrinėjama sorbcinio metodo taikymo sunkiesiems metalams šalinti iš nuotekų galimybės, taip pat aprašomi sunkiųjų metalų sorbcijos iš vandens kinetikos tyrimai ir skaitinio modeliavimo taikymas sunkiųjų metalų sorbcijos iš vandens kinetikos proceso prognozei. Atlikti eksperimentiniai sunkiųjų metalų šalinimo iš nuotekų sorbentais efektyvumo priklausomybės nuo laiko tyrimai. Remiantis eksperimentinių tyrimų rezultatais, buvo sudaryti du pseudokinetiniai modeliai – pirmosios eilės ir antrosios eilės. Šie modeliai pritaikyti skaitiniame modeliavime, naudojant kompiuterinę programą *PHOENICS*. Atliekant skaitinį modeliavimą gauti sunkiųjų metalų sorbcijos iš vandens rezultatai palyginti su eksperimentinių tyrimų rezultatais. Palyginus abiejų pseudomodelių rezultatus nustatyta, kad pseudo- antrosios eilės modelis geriau atspindi sunkiųjų metalų sorbcijos iš vandens kinetiką.

Prasminiai žodžiai: sorbcija, sorbentai, sunkieji metalai, pseudokinetiniai modeliai, skaitinis modeliavimas.

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