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Features of sorption of lead (II) and cadmium (II) on carbon sorbent of wood nature

The carbon material of the wood nature modified with phosphoric acid with the subsequent carbonization at a temperature of 600 ºC was used as a sorbent. Protodyakonov's equations describing influence of all factors the generalized equations (pH, duration of contact of a sorbent with solution, initial concentration of metals' ions, temperature) on the sorption capacity of sorbent were obtained as a result of studying cadmium (II) and lead (II) ions' sorption. The analysis of these results allows concluding that sorption of lead (II) and cadmium (II) ions on sorbents occur rather actively. Also the calculation of basic thermodynamic and kinetic parameters of the sorption process was carried out.

Key words: sorption, sorbent, heavy metals, sorption capacity of a sorbent, sewage treatment.

Nowadays special attention focuses to the introduction of waste-free technology, especially sewage treatment. Protection of water resources from depletion and pollution and their rational using for the needs of the national economics, is one of the most important problems requiring urgent solutions. The probability of entering into the wastewater is high at using of lead in various industries (metallurgy, metal working, electrical, petrochemical, etc.). Consequently, the water pools are contaminated with the ions of lead, cadmium and other toxic metals exceeding the maximum permissible concentrations (MPC). It is known that limiting indicator of health hazard of lead is sanitary and toxicological. It suffices to note that lead and its derivatives are classified by International Agency for Research on Cancer (IARC) as 2B Group substance (potential human carcinogens) [1].

For ensuring environmental safety, i.e. to reduce and prevent the water basins' pollution the wastewater should be cleaned. The solution of this problem can be cleaning up using different sorbents [2]. Analysis of the literature on library databases http://elibrary.ru, http://scopus.com showed that nowadays the use of water treatment with natural sorbents based on wood materials is especially relevant.

The purposes of this research are investigation of sorption of lead (II) and cadmium (II) ions on carbon wood sorbent, and establishment of optimum conditions in a mode of static adsorption on the solid-liquid interface.

Experimental part

The carbon sorbent of the wood origin (dry cones of a pine ordinary (lat. Pínussylvéstris)) was used as a sorbent [3–5]. The sorbent was activated with 10 M solution of orthophosphoric acid with the subsequent carbonization at a temperature of 600 ºC; duration of processing is 1 hour, then the sorbent was washed out with distilled water and dried at 102–105 ºC up to the constant weight.

The sorption in relation to metal ions was carried out under static conditions according to the 4-factorial 3-level matrix [5], on the basis of the experiment the method of planning experiment was taken [6].

Initial concentration of model solutions of lead (II) and cadmium (II) were 25, 50, 100 mg/l; pH was varied in the range of 4–8, temperature interval varied from 298 K to 318 K, sorption duration were 30, 45, 60 min.

Discussion of results

As a result of investigation of sorption of cadmium (II) and lead (II) ions generalized Protodyakonov' equations [6] were obtained. They describe the influence of all factors (pH, duration of contact of sorbent with solution, initial concentration of metals' ions, temperature) on the sorption value:

– for Pb^{2+} ions:

$$a = \frac{\left(0.26\,\mathrm{pH}^2 - 3.03\,\mathrm{pH} + 63.64\right)\cdot\left(0.96C_{init} - 0.67\right)\cdot\left(-0.04T + 69.95\right)\cdot\left(-0.05\tau + 58.00\right)}{\overline{a}^3}; \quad (1)$$

– for Cd^{2+} ions:

$$a = \frac{\left(0.82\ln\mathrm{pH} + 53.73\right)\cdot\left(0.014C_{init}^{\,2} - 0.10C_{init} + 56.81\right)\cdot\left(-0.0015T^2 - 0.92T + 194.57\right)\cdot\left(0.96\tau - 0.77\right)}{\overline{a}^3}. \quad (2)$$

These equations allow predicting the sorption capacity of a studied sorbent in relation to metals at a variation of the above said factors.

As a result of calculations it was established that in case of lead (II) ions sorption minimum value of purification degree is 93.14 % under conditions of pH = 4, initial concentration of the sorbent 25 mg/l, contact time is 60 min. and temperature 298 K; whereas the maximum of purification degree (99.11 %) from lead (II) ions is observed in sorption process under following conditions: pH = 8, T = 298 K, C_{init} = 100 mg/l, τ = 60 min.

The analysis of experimental data obtained on sorption of cadmium (II) ions on active coals on the basis of modified coniferous wood have shown, that the maximum purification degree (90.86 %) is reached when sorption cleaning carrying out at pH = 8, initial concentration 100 mg/l, contact time 60 min and temperature 298 K.

Sorption capacity of the sorbent in relation to lead (II) and cadmium (II) ions was studied in dependence on pH in static conditions. Dependence of sorption capacity of lead (II) and cadmium (II) ions on solution pH is given in figure.

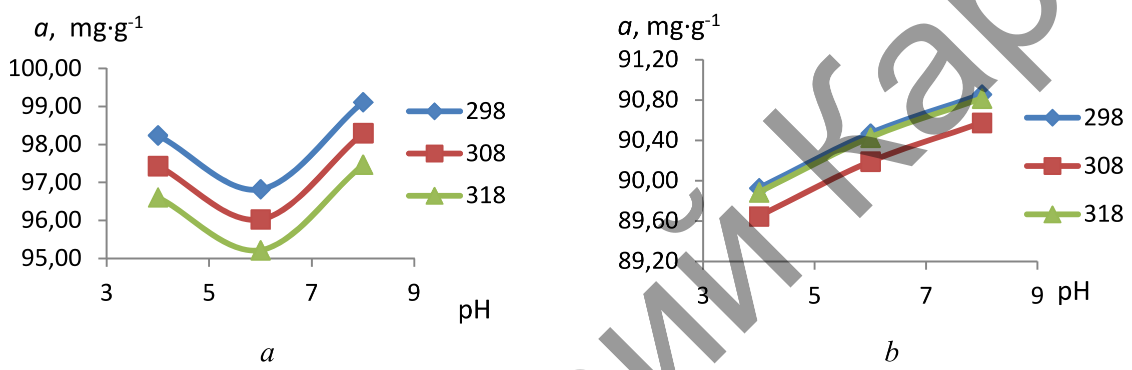

Figure. Sorption capacity of sorbent in relation to lead (II) (*a*) and cadmium (II) (*b*) ions in dependence on pH; initial concentration of metal is 100 mg/l

As seen from figure, the sorption curve of metal ions passes through a minimum, with decreasing acidity in the range of pH = 4÷9, reaches a minimum at a value of pH equal to 6 and, then, increases. The most optimum pH of medium is 8. Lead is sorbed in the form of $PbOH^{+}$ ion at pH ≥ 8. Such ions have a smaller charge and bigger radiuses, and smaller hydration degree. So they enter easily into electrostatic interactions and an ionic exchange in comparison with Pb^{2+} ion.

In case of cadmium (II) ions the sorption capacity of sorbent increases with rising medium acidity. A relatively small degree of sorption in more acidic mediums (pH <5) is caused, presumably, by the fact that sorbent in this medium is in the protonated state; sorption proceeds as a result of coordinating interaction with the P = O groups.

However, these groups also absorb protons, due to the formation of hydrogen bonds –P=O ···· H+, it leads to replacement of lead ions. In this interval of acidity of water solutions the cadmium ions are in a form of aqua complexes ($[Cd(H_2O)_n]^{2+}$). Thus, results show that slightly alkaline medium (pH 8) is the most favorable for occuring the sorption process. Accordingly, all further investigations were carried out at the optimum value of pH (pH = 8).

Isotherms of sorption were recalculated in isotherms of the Lengmyur's equation in a rectilinear form, and sorption constants (K) at temperature of 298, 303 and 318 K were calculated. On the basis of sorption constants the enthalpy change (ΔH), isobaric-isothermal potential (ΔG) and entropy changes (ΔS) were calculated:

$$\Delta H = \frac{RT_iT_k \ln\left(\frac{K_i}{K_k}\right)}{T_i - T_k}; \qquad (3)$$

$$\Delta G_i = -RT_i \ln K_i; \qquad (4)$$

$$\Delta S_i = \frac{\Delta H - \Delta G_i}{T_i}\,. \tag{5}$$

Results of calculations are given in Table 1.

T a b l e 1

The basic characteristics of sorption of lead (II) and cadmium (II) ions on the sorbent obtained on the basis of coniferous wood

Determined characteristic	Tempera-ture, K	Sorption of ions	
		Pb^{2+}	Cd^{2+}
Constants of sorption	298	1.083	1.191
	308	1.091	1.192
	318	1.101	1.194
–Δ*G*, kJ/mole	298	0.19	0.43
	308	0.22	0.44
	318	0.25	0.47
–Δ*H*, kJ/mole	–	0.63	0.09
–Δ*S*, J·mole/K	298	1.46	0.67
	308	1.33	0.60
	318	1.19	0.52

The analysis of the results obtained allows concluding that sorption processes of lead (II) and cadmium (II) ions on sorbents occur rather actively. The negative values of enthalpy and isobaric-isothermal potential indicate on spontaneous nature of sorption process. The results have shown, that the formation of strong adsorptive complexes had occurred, thus capacity of sorbents in relation to heavy toxic metals is sufficiently high, therefore, allows to extract large amount of metals from water in wide range of temperatures [7].

Further the calculation of distribution coefficient *D* at pH at which maximum sorption was made (Table 2):

$$D = \frac{C_{sorp} \cdot V_{sol}}{m_{sorp} \cdot C_{res}}\,, \tag{6}$$

where C_{sorb} is amount of metal ions in sorbent phase (mg/l); V_{sol} is volume of water phase (ml), m_{sorb} is mass of sorbent (g), C_{res} is amount of not sorbed metal ions after sorption.

T a b l e 2

Change of Distribution Coefficients D (initial concentration of metals ions is 100 mg·L^{-1})

T, K	Pb^{2+}	Cd^{2+}
298	5584.82	496.85
308	2890.63	480.45
318	1925.53	494.36

The greatest values of distribution coefficient (>500) are attained for Pb^{2+} ions. The distribution coefficients show that the sorbent can be used for concentration of lead (II) from solutions in static and dynamic conditions.

The time of establishment of sorption balance is necessary for the characteristic and the description of equilibrium processes, and the value of entropy of activation is needed for the formation of activated complex, for mechanisms of sorption of lead (II) and cadmium (II) ions on sorbent.

As a result of investigation the rate constants of sorption, $S^{\#}$ and E_{act} of lead (II) and cadmium (II) ions on the modified sorbent at temperatures of 298, 308 and 318 K were calculated:

$$K = \frac{1}{\tau}\ln\frac{C_o}{C_i}\,, \tag{7}$$

where C_o is initial concentration of metal, mg/l, C_i is concentration of metal ions at time τ; τ — time, s.

The values of sorption energy (E_{act}) were calculated according to Arrhenius's graphes in coordinates of «ln K – 1/T», modification of formation entropy of sorption complexes ($S^{\#}$) were calculated by Eyring equation:

$$\ln PZ_0 = 10{,}36 + \ln T + \frac{\Delta S^{\#}}{R}, \qquad (8)$$

where PZ_0 is preexponential factor in Arrhenius equation; $\Delta S^{\#}$ is the modification of formation entropy of sorption complexes; R — gas constant; T — temperature, K.

Results of calculations of constants of sorption kinetics, E_{act} and $S^{\#}$ of lead (II) and cadmium (II) ions using modified sorbent are given in Table 3.

Table 3

Thermodynamic characteristics of kinetics of sorption of lead (II) and cadmium (II) ions

Determined characteristic	Temperature, K	Sorption of ions	
		Pb^{2+}	Cd^{2+}
Rate constants $K \cdot 10^{-3}$, s^{-1} at temperatures, K	298	0.66	3.53
	308	0.86	4.33
	318	1.07	4.33
E_{act}, kJ/mole	in the range of 298 K to 318 K	18.65	8.20
$-\Delta S^{\#}$, J/mole·K	298	74.24	95.20
	308	74.51	95.48
	318	74.77	95.74

Practically all studied sorption curves have reasonably steep initial portion of isotherms of sorption kinetics. Apparently from the results of experiments, the sorption is sufficiently fast and ends in 30 min. This allows concluding that all sorbate adsorbed on the sorbent.

Conclusion

Thus, the results indicate on high efficiency of using the sorbent formed on the basis of coniferous wood with the subsequent modification for sewage treatment from heavy toxic metals, such as lead and cadmium, with purification degree to 99 %.

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Ағаш негізіндегі көміртекті сорбенттегі қорғасын (II) мен кадмий (II)-ге қатысты сорбцияның ерекшеліктері

Сорбент ретінде ортофосфор қышқылымен модифицирленген, 600ºС температурада кезекті карбонизацияға ұшыраған ағаш негізіндегі көміртекті сорбент қолданылды. Қорғасын (II) мен кадмий (II) иондарына қатысты сорбцияны зерттеу нәтижесінде сорбенттің сорбциялық сыйымдылығына әсер ететін барлық факторларды (pH, сорбенттің ерітіндімен байланыс ұзақтығы, металл иондарының бастапқы концентрациялары, температура) қамтитын Протодьяконовтың жалпы теңдеуі алынды. Зерттеу нәтижелері қарастырылып отырған сорбенттің қорғасын мен кадмий иондарына қатысты сорбциясы белсенді екенін көрсетті. Сонымен қатар сорбция процесінің негізгі термодинамикалық және кинетикалық көрсеткіштерінің есептеу нәтижелері берілді.

Ш.К.Амерханова, Р.К.Жаслан, А.С.Уали

Особенности сорбции свинца (II) и кадмия (II) на углеродном сорбенте древесной природы

В качестве сорбента был использован углеродный сорбент древесной природы, который был модифицирован ортофосфорной кислотой с последующей карбонизацией при температуре 600 °С. В результате изучения сорбции ионов кадмия (II) и свинца (II) были получены обобщенные уравнения Протодьяконова, описывающие влияние всех факторов (pH, продолжительность контакта сорбента с раствором, исходная концентрация ионов металлов, температура) на сорбционную емкость сорбента. Анализ полученных результатов позволил сделать вывод о том, что сорбция ионов свинца и кадмия на рассматриваемых сорбентах идет достаточно активно. Также был проведен расчет основных термодинамических и кинетических параметров процесса сорбции.

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