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The concentration of cadmium (II), lead (II) and mercury (I, II) ions by adsorption on the wood-modified sorbent

This article discusses the results of FT-IR spectroscopy, X-ray diffraction, and sorption properties of activated carbons from dry pine cones common in relation to of Cd (II), Pb (II), Hg (I, II) ions. The results indicate the higher efficiency of the sorbent that is based on softwood followed by modification for wastewater treatment from toxic heavy metals such as lead, cadmium and mercury with purity from 90 % to 99 %.

Key words: pine cones, phosphoric acid, iodine adsorption capacity, adsorption, Cd (II), Pb (II), Hg (I, II) ions.

The problem of water purification from heavy metals continues to be relevant. Experts on environmental protection allocated priority group among metal-toxicants, it includes cadmium, copper, arsenic, nickel, mercury, lead, zinc and chromium as the most dangerous to human and animal health. Among them mercury, lead and cadmium are the most toxic [1–3].

Additional techniques have been successfully applied for wastewater purification can be called sorption after treatment using porous materials. And recently, the possibility of replacing expensive unconventional adsorbents of available and cheap materials, both artificial and natural origin, is researched. For such materials, developed specific surface area of the high absorbency pairs, liquids and solutes is characterized; they can serve as carriers for mounting on the surface of various compounds for their modification. Widespread sorbents also include activated carbons that may be derived from wood, lignite and coal, etc.

The large share of plant material, growing in the territory of central and northern Kazakhstan and Siberia (Russia), consists of coniferous trees (pine, spruce, fir), which are waste bark, cones, and others.

The aim of this work is to obtain the carbon-based sorbent softwood and its use in the sorption concentration of cadmium (II), lead (II) and mercury (I, II).

Experimental part

As a raw material it was used crushed mass (0.5–2 mm) obtained on the basis of the dry residue (cones) of softwood which humidity is 8 % [4], the volatile content is 12.2 % [5].

Modification of the feedstock was carried out by impregnation with a modifier followed by stirring at constant temperature of 70 °C. The weight ratio of raw material to the modifier is 1:5. As the modifier a solution of phosphoric acid (10 $\text{mole}\cdot\text{L}^{-1}$) was used. Evaporation leads to the formation of wet residue. Thermal treatment was carried out at temperatures of 200, 300, 400, 500, 600, 700, 800 ºC at a rate of temperature increase of 10 $°\text{C}\cdot\text{min}^{-1}$ and holding at final temperature for 60 minutes. After heat treatment, the carbonized material obtained was washed with distilled water (3 times) and dried at 105 ºC.

Investigation of the porous structure and the specific surface was performed on gas adsorption analyzer TriStar II.

FT-IR spectroscopic analysis of the samples was conducted on the FSM 1201 device.

X-ray diffraction analysis was performed by DRON-2.

Determination of the sorption capacity for iodine were performed by as described [6]. Sorption with respect to metal ions was carried out under static conditions by the method of [7] based on the method of the experiment planning [8].

The initial concentration of metal ions was 25, 50, 100 $\text{mg}\cdot\text{L}^{-1}$. Solutions of metal ions were prepared from the reagents of the brand «analytical grade» in bidistilled water.

Discussion of the results

It has been established that the moisture of adsorbent is 8 % and volatile content is 12.2 %.

FT-IR spectroscopy technique was used for the analysis of samples of the sorbent before and after modification (Fig. 1) in order to identify the functional groups existing on the surface of the sorbent.

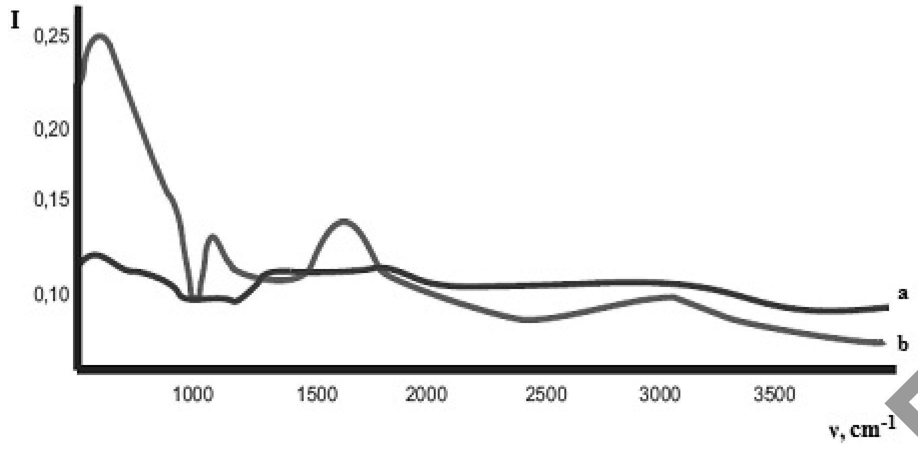

Figure 1. FT-IR-spectrum of the initial material (*a*), carbonized modified sorbent (*b*)

In the FT-IR spectra of the modified sorbent absorption bands at 1085, 1571 and 3117 cm^{-1} were registered. Intense band in the region 1580–1660 cm^{-1} corresponds to stretching vibrations of C=C bonds of the aromatic rings, although in this area in some cases olefinic C=C bond included in the linear system of conjugation can absorb. Absorption peak at 3117 cm^{-1} can be attributed to the stretching vibrations of aromatic C–H bonds. Absorption in the 1085 cm^{-1} indicates the presence on the surface of the sorbent inorganic ions PO_4^{2-}, HPO_4^- indicating that passage of the modification process sorbent phosphate ions (Fig. 1).

The results of studies of porosity and specific surface. In the case of heat treatment at a sorbent has elapsed 800 °C specific surface area was 870 $m^2 \cdot g^{-1}$, a total pore volume is 0.09 $cm^3 \cdot g^{-1}$, average pore size is 3.7 nm, hence the sorbent being studied can be classified as a mesoporous one.

XRD analysis of the modified materials showed that treatment of the starting material with phosphoric acid, followed by carbonization facilitates formation of amorphous carbon, which upon heat treatment forms a porous carbon material. It can be seen from the wide smooth hillocks 5 to 30º degrees of diffraction, which is also characteristic of the amorphous material. From this it follows that during the carbonization of cellulose crystal structure, one of the components of wood material, becomes an amorphous, disordered structure, capable of adsorption (Fig. 2).

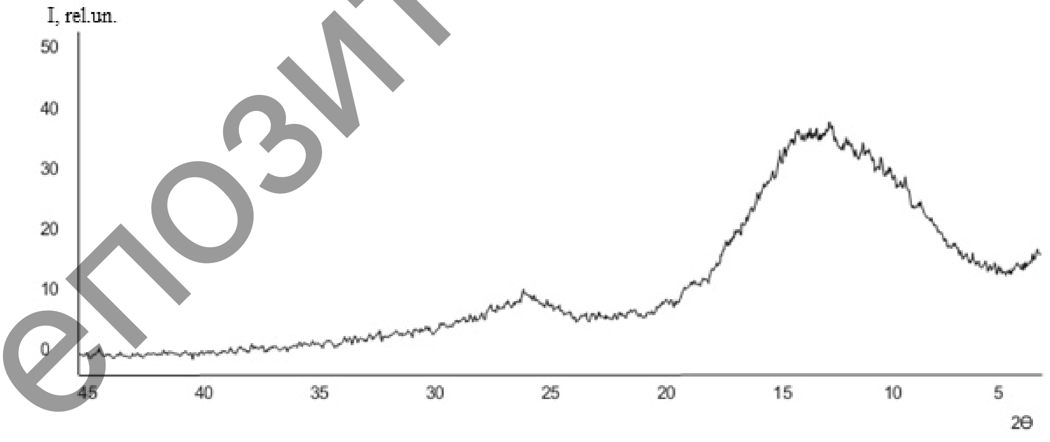

Figure 2. Diffractogram of the modified sorbent

Further the investigation of the sorption properties of the sorbent with respect to iodine was carried out. The results are shown in Figure 3.

It is established that the most of the sorption capacity of the sorbent has an iodine heat treated at 800 ºC.

Adsorption of Pb^{2+}, Cd^{2+} ions on carbon sorbents from model solutions. The investigations of sorption capacity of the sorbent prepared for Pb^{2+}, Cd^{2+} ions under static conditions were conducted.

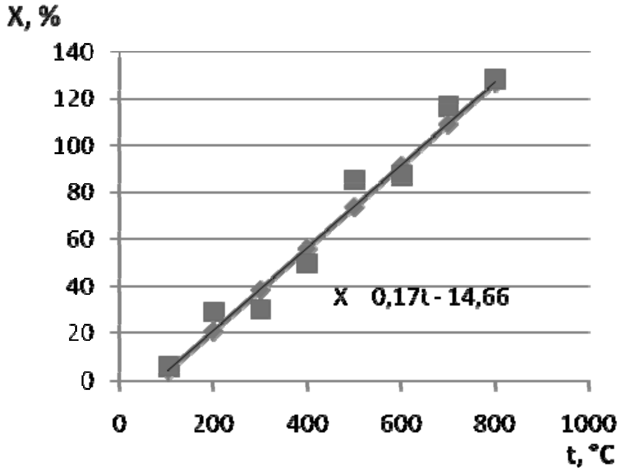

Figure 3. Dependence of the sorption capacity of the sorbent with respect to iodine from heat treatment temperature

Experiments to study the sorption under static conditions were carried out by the method of mathematical planning, the results of which were obtained by the generalized equations of Protodyakonov [8] describing influence of all factors: pH, contact time of sorbent with solution, initial concentration of metal ions (Table 1).

Table 1

Equations of Protodyakonov describing the influence of all factors (pH, contact time of sorbent with solution, initial concentration of metal ions)

Ions	Equations
Pb^{2+}	$a=\dfrac{(0.01pH^2-0.15pH+5.26)\cdot(-2E-05C_{init}^2+0.48\cdot10^{-2}C_{init}+4.68)}{\overline{a}^3}\times$ $\times\dfrac{(-0.1\cdot10^{-3}T^2+0.09T-8.56)\cdot(-1E-04\tau^2+6.1\cdot10^{-3}\tau+4.80)}{\overline{a}^3}$
Cd^{2+}	$a=\dfrac{(-1.10\cdot10^{-3}pH^2+0.02pH+4.76)\cdot(7E-05\tau^2-5.2\cdot10^{-3}\tau+4.92)}{\overline{a}^3}\times$ $\times\dfrac{(-6E-05C_{init}^2+9{,}10\cdot10^{-3}C_{init}+4.56)\cdot(8E-05T^2-46.30\cdot10^{-3}T+11.81)}{\overline{a}^3}$
Hg^{2+}	$a=\dfrac{(24.00\cdot10^{-3}pH^2-0.28pH+5.66)\cdot(4.10\cdot10^{-3}\tau+4.72)}{\overline{a}^3}\times$ $\times\dfrac{(-4E-05C_{init}^2+6.40\cdot10^{-3}C_{init}+4.72)\cdot(-0.5\cdot10^{-3}T^2+0.32T-45.03}{\overline{a}^3}$
Hg^{+}	$a=\dfrac{(5.90\cdot10^{-3}pH^2-0.07pH+5.13)\cdot(-9E-05\tau^2+0.01\tau+4.67)}{\overline{a}^3}\times$ $\times\dfrac{(-2E-05C_{init}^2+2{,}00\cdot10^{-3}C_{init}+4.89)\cdot(0.40\cdot10^{-3}T^2-0.26T+45.35}{\overline{a}^3}$

The above equations are possible to predict the sorption capacity of the sorbent being studied by varying the above factors. In the table below (Table 2) the optimal conditions for the heavy metal ions and the value of adsorption at these conditions are presented.

Table 2

Optimal conditions for the concentration of heavy metals and sorption value

Ions	pH	Contact time, min	C_{init}, mg·L^{-1}	Temperature, K	Sorption value, *a*, mg·g^{-1}
Pb^{2+}	8	30	100	318	10.18
Cd^{2+}	8	30	100	298	4.55
Hg^{2+}	4	30	100	298	3.89
Hg^{+}	4	30	100	298	4.46

As a result of calculations it is established that in the case of the sorption of lead (II) the minimum value of the degree of purification is 93.14 % under the conditions of pH = 4, the initial concentration of sorbate is 25 mg·L^{-1}, a contact time is 60 min and a temperature of 298 K, while the maximum purity (99.11 %) of lead (II) ions is observed in the adsorption purification process under the following conditions that are pH = 8 and T = 298 K, C_{init}=100 mg·L^{-1}, τ = 60 min.

Analysis of the experimental data obtained by the sorption of cadmium (II) ions on activated carbons based on the modified softwood, shows that the maximum degree of purification (90.86 %) achieved during the sorption concentration at pH = 8, the initial concentration of sorbate is 100 mg·L^{-1}, contact time is 60 min and a temperature of 298 K.

The maximum purification degree of model solutions of wastes from of mercury (I, II) ions under the optimal conditions is about ≈97.50 %.

The sorption capacity of the sorbent with respect to the lead (II) and cadmium (II) ions was studied as a function of pH under static conditions. With decreasing of pH of solutions in range pH = 4÷9 sorption of ions passes through a minimum, reached a minimum at pH~6 and equal, then increases. Most optimum pH is 8. Lead (II) ions sorbed in the form of $PbOH^+$ at pH ≥ 8. Such ions because of the smaller and larger radius of charge and the degree of hydration less easily enter the electrostatic interactions and ion exchange with adsorbent surface in comparison with Pb^{2+} ion [9].

For cadmium (II) ions the sorption capacity of the sorbent increases when acidity of the medium increases. A relatively small degree of sorption in more acidic environments (pH < 5) is caused, presumably, the fact that in this pH region the sorbent is in the protonated state and adsorption occurs as a result of interaction with the coordinating P = O groups. However, these groups are also absorbed protons due to the formation of hydrogen bonds, $P = O \bullet \bullet \bullet \bullet H^+$, resulting in the displacement of lead ions. In this pH range of aqueous solutions of cadmium ions are in the form aqua complexes ($[Cd(H_2O)n]^{2+}$). Thus, the results show that slightly alkaline pH 8 is the most favorable for the occurrence of the sorption process.

Figure 4 presents a diagram showing the comparative analysis of heavy metal ions on the degree of purification in the investigated sorbent.

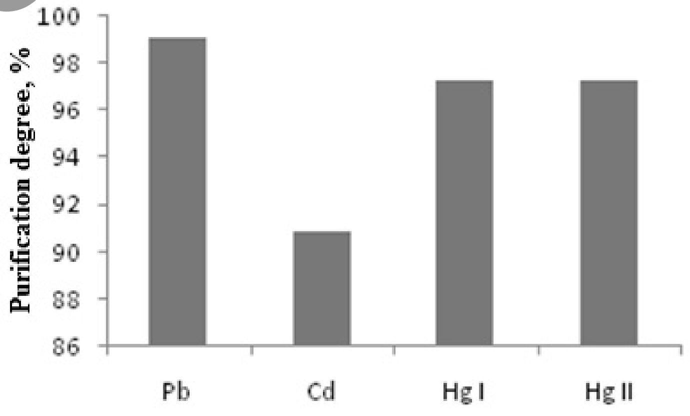

Figure 4. The comparative analysis of purification degree of heavy metal ions

Thus, as a result of experimental study of the adsorption processes occurring at concentration of heavy metals ions from model solutions, it is found that from all of these metals the investigated sorbent has the highest sorption capacity with respect to the lead ions.

The integral kinetic curves of sorption are presented on the Figure 5.

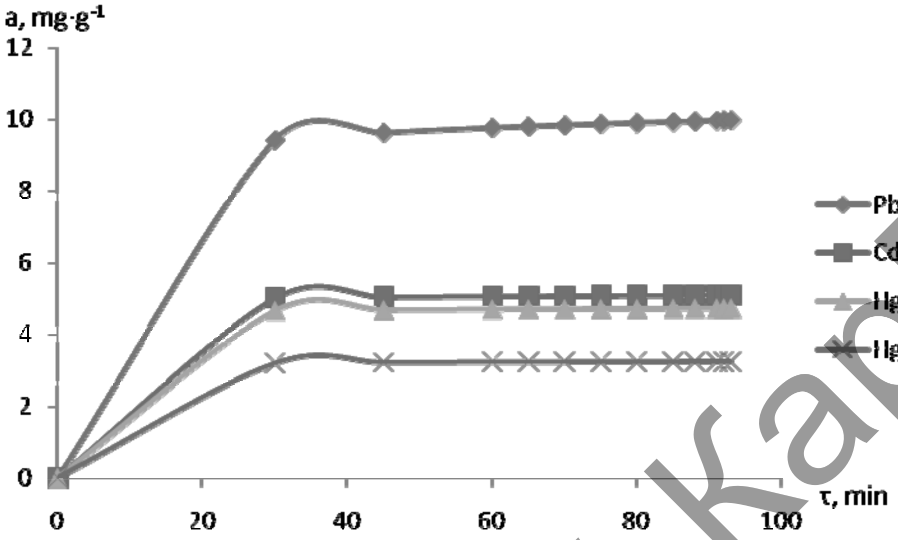

Figure 5. Integral kinetic curves of sorption of metals on wood carbonized sorbent

As seen in Figure 5, the total sorption equilibrium is achieved at all temperatures after 45 minutes of contact. According to the literature [10], this suggests that several steps determine the rate of the sorption process. The data were processed by the method of Boyd [11] for determination of sorption process mode (external or internal diffusion). The convex dependence F — $\tau^{1/2}$ also shows that the rate-limiting step of the sorption of metals is external diffusion.

Next the dependence of –ln(1–F) from τ is constructed. In our conditions, a linear portion of the entire time interval at all temperatures is fixed. Thus, the main limiting process is external diffusion. The Boyd model based on the fact that the ion exchange step occurs substantially instantaneously and can't control the speed of the overall process.

To identify the contribution of the chemical stage in the overall speed of the process of sorption kinetic curves were processed by applying a pseudo-model of the first order. Parameters calculated based on the integral curve using kinetic models of pseudo-first order, the results are presented in Table 3.

Table 3

Equation of pseudo-first order model of chemical kinetics and the rate constant of adsorption process, the initial concentration is 100 mg·g^{-1}, 298 K

Metal ions	Equation	*a*, mg·g^{-1} (exp)	*a*, mg·g^{-1} (calc)	Rate constant $k_1 \cdot 10^{-2}$ (min^{-1})
Pb^{2+}	$a_t = a_c\left(1 - e^{-k_1 t}\right)$	11.00	11.16	k_1=3.23
Cd^{2+}		7.00	8.15	k_1=1.51
Hg^{+}		6.00	6.48	k_1=2.00
Hg^{2+}		5.00	7.06	k_1=0.95

From the data presented in Table 3 and in Figure 5 it is seen that in this case the sorption of metals is well described by the pseudo-first order. It should be noted that the model equation of pseudo-first-order equation is identical to the diffusion membrane. However, in the case of diffusion rate in the film depends on the size of the sorbent particles and the film thickness.

Thus, in the case when the kinetics of the process is described by the pseudo-first order, diffusion precedes sorption.

Thus, the results clearly indicate the higher efficiency of the sorbent that is based on softwood followed by modification, for wastewater treatment from toxic heavy metals such as lead, cadmium and mercury, with purity from 90 % to 99 %.

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Ш.К. Амерханова, Р.М. Шляпов, А.С. Уали, М.С. Татибаева

Кадмий (II), қорғасын (II) және сынап (I, II) иондарын түрлендірілген ағаш сорбентіндегі адсорбциясы арқылы шоғырландыру

Мақалада Cd(II), Pb(II), Hg(I, II) иондарының қатысында ИК-Фурье-спектроскопиялық, рентгенофазалық талдау, сонымен қатар кәдімгі қарағайдың құрғақ бүрлерінің негізінде белсенді көмірлерді сорбциялық қасиеттерінің нәтижелері талқыланды. Алынған нәтижелер кадмий және сынап, қорғасын сияқты ауыр уытты металдардан ағынды суларды тазартуда қылқан жапырақты ағаштың негізінде құрылған сорбенттің жоғары тиімділігін анықтап, тазарту дәрежесі 90–99 % аралығында жататынын көрсетті.

Ш.К. Амерханова, Р.М. Шляпов, А.С. Уали, М.С. Татибаева

Концентрирование ионов кадмия (II), свинца (II) и ртути (I, II) путем адсорбции на модифицированном древесном сорбенте

В статье приведены результаты ИК-Фурье-спектроскопического, рентгенофазового анализа, а также исследований сорбционных свойств активных углей из сухих шишек сосны обыкновенной по отношению к ионам Cd (II), Pb (II), Hg (I, II). Результаты свидетельствуют о высокой эффективности использования сорбента, созданного на основе хвойной древесины с последующей модификацией, для очистки сточных вод от тяжелых токсичных металлов, таких как свинец, кадмий и ртуть, со степенью очистки от 90 % до 99 %.

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