Effect of Temperature on the Kinetics of Sorption of Co²⁺ and Ni²⁺ Ions by a Sorbent Based on an Inositol Hexaphosphoric Acid Derivative

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Abstract—Data on the effect temperature has on the kinetics of the removal of Co²⁺ and Ni²⁺ ions under static conditions by a sorbent based on a derivative of phytic acid fabricated from rice production waste are presented. It is shown that when the temperature is raised from 20 to 60°C, the sorption capacity of the sorbent based on phytic acid increases over the period of sorption and within 180 min reaches values of 1.4 mmol g^{-1} for Co²⁺ ions and 1.3 mmol g^{-1} for Ni²⁺ ions. It is established that for the investigated range of temperatures, order n of the sorption of Co²⁺ and Ni²⁺ ions is <1, which characterizes the reactions accompanied by diffusion processes. It is found that the process of removal of Co²⁺ and Ni²⁺ ions is characterized with low activation energy (20.74 kJ mol^{-1} for Co²⁺ ions and 14.2 kJ mol^{-1} for Ni²⁺ ions). It is also demonstrated that the sorption process in the considered time frame is best described by a kinetic model of a pseudo-second order, as is indicated by respective correlation coefficients.

Keywords: rice production waste, phytic acid salts, sorbents, sorption kinetics, heavy metal ions

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INTRODUCTION

Inositol hexaphosphoric acid (IHPA, phytic acid) is a typical product of vegetable origin, but its composition and structure can differ, depending on the raw materials and their processing means [1]. It comprises an ester of the cyclic hexaatomic alcohol (*myo*-inositol) and six residues of phosphoric acid of a general formula $C_6H_6[OPO(OH)_2]_6$. It is worth noting that IHPA might not contain all six phosphoric acid residues, but only two, three, four, or five phosphorus-containing groups [2, 3]. Due to multistage dissociation, orthophosphoric acid residues can serve as acceptors or donors of up to 12 protons, allowing IHPA to behave as a highly active polydentate ligand capable of chelate cations through the formation of a network of coordination bonds [4].

The interest in complex compounds containing IHPA and its derivatives in the form of ligands has continued on the same level for decades. Authors worldwide have described IHPA complexes with alkali (Li, Na, K, Cs) [5, 6], alkali-earth (Ca, Mg) [7], and other (Zn, Cu, Co, Mn, Cd, Pb, Hg, Ni, Sn, Fe) metals [8–10].

The capacity of IHPA and its salts to chelate metal cations efficiently allows us to consider them sorbents of heavy metal ions from aqueous solutions. Studies on the use of IHPA and its derivatives, and of materials based on them, in decontaminating aqueous solutions of heavy metals are under way in Australia, Sweden, Italy, and Turkey [11–15].

The kinetics of sorption of heavy metal ions (Co²⁺, Sr²⁺, Pb²⁺, Cd²⁺, Zn²⁺, Ni²⁺, Cu²⁺, and Mn²⁺) by a sorbent based on an IHPA derivative (referred to below as a phytic sorbent) produced from rice processing byproduct (rice bran) was investigated at the Russian Academy of Sciences' Institute of Chemistry in Vladivostok. It was found that the equilibrium in the distribution of metal ions between the solution and the sorbent was established within 4 min for Pb²⁺ ions, within 16 min for Zn²⁺ ions, within 30 min for Cu²⁺ ions, within 60 min for Cd²⁺ and Sr²⁺ ions, and within 120 min for Mn²⁺, Co²⁺, and Ni²⁺ ions. The highest values of the degree of removal (99.7–97.4%) under equilibrium conditions were observed upon the sorption of Pb²⁺, Zn²⁺, Cu²⁺, and Cd²⁺ ions. It was found that in all cases, the kinetics of sorption of heavy metal ions was best described by a kinetic model of pseudo-second order [16, 17].

The aim of this work was to study the effect temperature has on the kinetics of the removal of Co^{2+} and Ni^{2+} ions by a phytic sorbent.

EXPERIMENTAL

Fabrication Sorbent Based on an IHPA Derivative (a Phytic Sorbent)

Rice bran with a particle size of 0.3 mm was used as our initial raw material. The bran was obtained by grinding grains of rice grown in Timiryazevskii township (Primorskii Krai).

To fabricate a sorbent based on a phytic acid derivative, the rice bran was subjected to acidic hydrolysis with 0.27 M hydrochloric acid, and the resulting solution was sent for ultrafiltration. The IHPA derivative was precipitated from the purified extract by 2.75 M sodium hydroxide, as was described in [18].

Sorption Experiments

Our kinetic experiments were performed under static conditions at 20, 40, and 60°C using aqueous solutions of cobalt and nickel chlorides with stirring by an RT 15 Power magnetic stirrer (IKA WERKE, Germany) with a controlled heating temperature. Solutions of corresponding cobalt and nickel salts of specified concentrations were prepared via the dissolution of accurately weighed samples of $CoCl_2 \cdot 6H_2O$ of analytical grade (Russian State Standard GOST 4525-77) and $NiCl_2 \cdot 6H_2O$ of chemically pure grade (GOST 4038-79) in distilled water. Sorbent samples (0.05 g each) were placed into a series of test tubes with 20 mL of aqueous solutions of salts of the corresponding metals with initial ion concentrations of 200 μg mL^{-1}, and stirred at a specific temperature for different time periods (1 to 180 min). At different times, the solution was separated from the sorbent by filtering and analyzed for the respective ions.

The sorption capacity (A_s, mol g^{-1}) of the phytic sorbent was calculated using the formula

$$A_s = \frac{(C_{init} - C_{eq})}{m}V,\qquad(1)$$

where C_{init} is the initial concentration of the metal ion in solution, mol L^{-1}; C_{eq} is the equilibrium concentration of the metal ion in solution, mol L^{-1}; V is the solution volume, L; and m is the sorbent weight, g.

The degree of metal removal (α, %) was calculated according to the formula

$$\alpha = \frac{(C_{init} - C_p)}{C_{init}} \times 100\%.\qquad(2)$$

Time dependences of the sorption capacity were analyzed using the Kolmogorov−Erofeev equation

$$\alpha = 1 - [\exp(-kt^n)],\qquad(3)$$

where α is the degree of completeness of the cationic exchange reaction in the process of sorption; k is the constant characterizing the reaction rate; t is the sorption time; and n is the reaction order [19].

The kinetic data on metal ion sorption were also analyzed using kinetic models of pseudo-first and pseudo-second orders [20, 21].

The kinetic equation of pseudo-first order (Lagergren equation) is

$$dA_t/dt = k_1(A_e - A_t),\qquad(4)$$

where k_1 is the sorption rate constant for the model of pseudo-first order; A_e, A_t is the sorption capacity in the equilibrium state and at moment t, respectively.

Under initial conditions ($A_t = 0$ at $t = 0$ and $A_t = A_t$ at moment $t = t$), the equation's linear integral form can be written as

$$\log(A_e - A_t) = \log A_e - \frac{k_1}{2.303}t.\qquad(5)$$

The kinetic model of pseudo-second order is

$$dA_t/dt = k_2(A_e - A_t)^2,\qquad(6)$$

where k_2 is the sorption rate constant for the model of pseudo-second order.

Expression (6) can be transformed as

$$\frac{t}{A_t} = \frac{1}{k_2 A_e^2} + \frac{1}{A_e}t.\qquad(7)$$

Methods of Analysis

An analysis using a set of sieves was performed to determine the average size of rice bran particles. The sieve sizes (in μm) were 0.071, 0.100, 0.160, 0.200, 0.250, and 0.315. Fractionation was performed using an Analysette 3 Spartan Fritsch vibro-disperser (Germany) for 15 min. The weights of the fractions retained on the sieves were determined using a Gosmetr VLTE-1100 technical balance (Russia).

The average size of a grain on a sieve in the ground material was calculated using the technique proposed in [22].

The XRD patterns of substances were recorded using a Bruker D8 ADVANCE X-ray diffractometer (Germany) in CuK_α radiation; the obtained patterns were identified using the EVA program with the PDF-2 powder database [23].

Energy-dispersive X-ray fluorescence using a Shimadzu EDX 800 HS spectrometer (Japan) was used for quantitative determination of a sample's elemental composition. Analysis was performed without considering light elements. The concentrations of elements to be determined were calculated according to the method of fundamental parameters using the spectrometer's software. The relative error of determination did not exceed ±2%.

IR absorption spectra of phosphorus-containing samples were registered in the range of 400–4000 cm^{-1} in petroleum jelly using a Shimadzu FTIR Prestige-21 Fourier IR spectrometer (Japan) at room temperature.

The samples' specific surface areas were determined by means of low-temperature nitrogen adsorption using a Sorbtometer-M device (Russia).

The contents of Co^{2+} and Ni^{2+} ions in solution were determined via atomic-absorption spectrometry using a SOLAAR M6 double-beam spectrometer (Thermo Scientific, United States) on analytical lines 240.7 and 232.0 nm, respectively.

RESULTS AND DISCUSSION

According to the XRD analysis data, the phosphorus-containing compound obtained from rice bran was X-ray-amorphous. The IR spectrum of the isolated product was characterized by the presence of two absorption bands in the range of stretching vibrations of PO_4 groups (993–996 and 1121–1128 cm^{-1}) and corresponds to the spectrum described in [24].

The quantitative determination of the element composition showed that the element ratio in the isolated phosphorus-containing product is P : C = 5.3–5.1 : 6, testifying to the presence of C_6P_5 fragments existing in pentaphosphoinositide in the investigated substances.

The specific surface area of the fabricated sample was 10.8 m^2 g^{-1}.

Figure 1 shows the kinetic curves of the sorption of Co^{2+} and Ni^{2+} by the phytic sorbent at 20, 40, and 60°C.

As can be seen from Fig. 1, at different temperatures we observe changes in the kinetics of Co^{2+} and Ni^{2+} removal. Along with the rise in temperature from 20 to 60°C, the sorption capacity of the investigated sorbent rose to 1.4 mmol g^{-1} for Co^{2+} ions and to 1.3 mmol g^{-1} for Ni^{2+} ions (the degree of removal of Co^{2+} ions was 92.1%; that of Ni^{2+} ions, 81.0%).

The data on sorption kinetics shown in Fig. 1 as dashed lines comprise the proposed empirical dependences, built using equation similar in form to the Langmuir equation:

$$A_t = A_m kt/(1 + kt), \quad (8)$$

where A_m is the maximum sorption capacity at a specified temperature, mol g^{-1}; k is a constant with dimension min^{-1} equal to the reciprocal value of the time of sorption at which the sorption capacity attains half the maximum value (determined from experimental data for each temperature). The experimental points of the values of the sorption capacity differ from the empirical ones by no more than 14%, which corresponds to
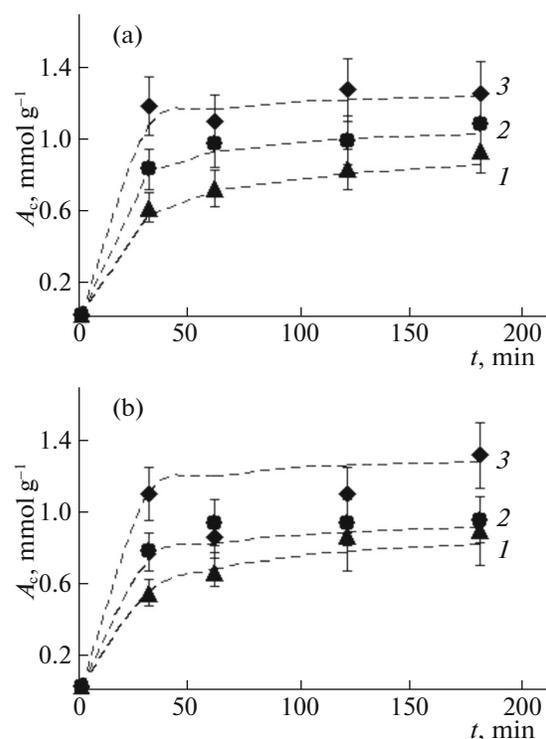

Fig. 1. Kinetic curves of the sorption of (a) Co^{2+} and (b) Ni^{2+} by phytic sorbent at different temperatures: (*1*) 20, (*2*) 40, and (*3*) 60°C.

the error of determining the concentrations of the investigated ions.

Figure 2 shows the experimental data on the sorption kinetics in the form of logarithmic dependences using Kolmogorov−Erofeev equation (3) after finding the second logarithm:

$$\ln(-\ln(1 - \alpha)) = \ln k + n\ln t. \quad (9)$$

The linear dependences observed in logarithmic coordinates testify to constant n in the specified time inter-

Table 1. Reaction order n and rate k obtained by analyzing the kinetic data according to the Kolmogorov−Erofeev equation

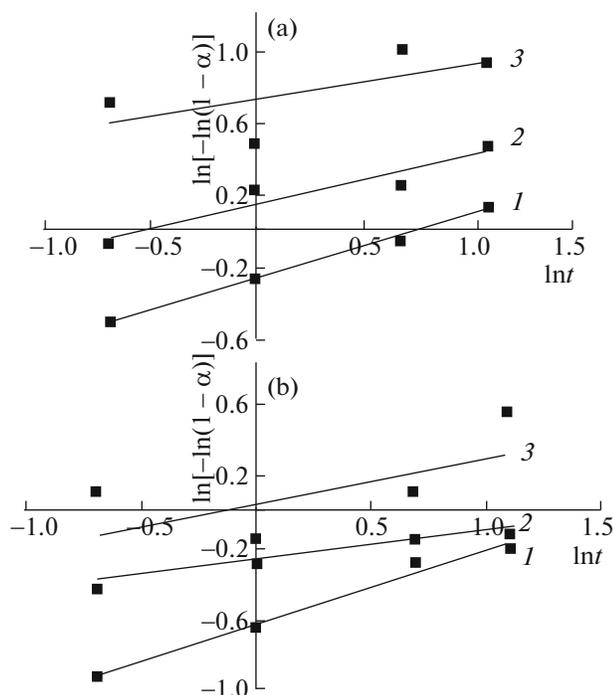| Ion	T, °C	n	k, min^{-n}	R^2
Co^{2+}	20	0.3484	0.76	0.9944
	40	0.2617	1.16	0.8945
	60	0.1941	2.06	0.4339
Ni^{2+}	20	0.4201	0.52	0.9881
	40	0.1638	0.76	0.7326
	60	0.2529	1.03	0.3368

Fig. 2. Logarithmic dependences $\ln[-\ln(1 - \alpha)]$ on time ($\ln t$) at different temperatures: (*1*) 20, (*2*) 40, and (*3*) 60°C; (a) Co^{2+}, (b) Ni^{2+}.
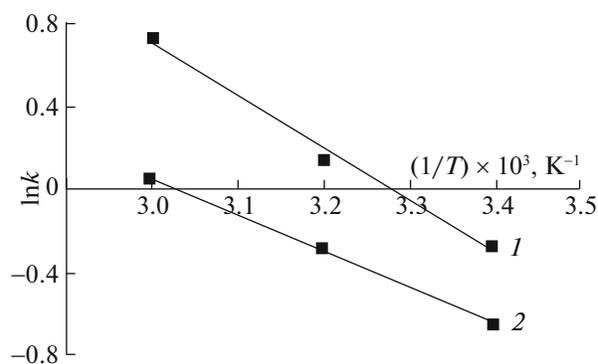

Fig. 3. Temperature dependences of the reaction constant logarithm ($\ln k$) upon ion removal: (*1*) Co^{2+}, (*2*) Ni^{2+}.

vals. The kinetic data processed using the generalized topochemical equation are shown in Table 1.

As can be seen from Table 1 in the analyzed temperature range, order n of the sorption of Co^{2+} and Ni^{2+} ions was <1, which characterizes reactions accompanied by diffusion processes.

Table 2. Results from processing kinetic curves of the sorption of Co^{2+} and Ni^{2+} ions by phytic sorbent using different chemical kinetic models

Ion	T, °C	pseudo-first order		pseudo-second order	
		$k_1 \times 10^{-2}$, min^{-1}	R^2	k_2, g mmol^{-1} min^{-1}	R^2
Co^{2+}	20	1.1	0.977	0.04	0.9943
	40	0.9	0.9019	0.07	0.9967
	60	1.2	0.6642	0.11	0.9962
Ni^{2+}	20	1.2	0.9633	0.03	0.9964
	40	0.71	0.6093	0.17	0.9990
	60	2.3	0.6921	0.03	0.9482

The energy of activation of the sorption of Co^{2+} and Ni^{2+} ions was graphically determined from the $\ln k$ values obtained using the temperature dependences (Fig. 2) using the Arrhenius equation in the logarithmic form,

$$\ln k = \ln A - Q/(RT), \tag{10}$$

where Q is the activation energy, R is the gas constant (8.3145 J mol^{-1} K^{-1}), and T is temperature. To determine the activation energy, the experimental data of $\ln k$ values are presented as dependences on reciprocal absolute temperature $(1/T)$ (Fig. 3) described by the linear equation $y = -2.4947x + 8.1816$ with regression coefficient $R^2 = 0.9915$ (for Co^{2+} ions) and linear equation $y = -1.7087x + 5.1688$ with regression coefficient $R^2 = 0.9976$ (for Ni^{2+} ions).

The energy of activation of sorption, calculated from experimental data, was 20.74 kJ mol^{-1} for Co^{2+} ions and 14.2 kJ mol^{-1} for Ni^{2+} ions. The above values are quite low, and these processes are characterized by negligible changes in the rate of cation exchange along with changes in temperature, as was corroborated experimentally.

The obtained data on the dependences of the sorption capacity on temperature and sorption time were also processed using pseudo-first and pseudo-second order models.

The apparent pseudo-rate constants (k_1 and k_2) and respective squares of correlation coefficients (R^2) indicating the correctness of the correlation with kinetic models of pseudo-first and pseudo-second order are shown in Table 2.

As follows from the data of Table 2, sorption in the analyzed time interval is best described by a model of pseudo-second order, as is indicated by respective correlation coefficients.
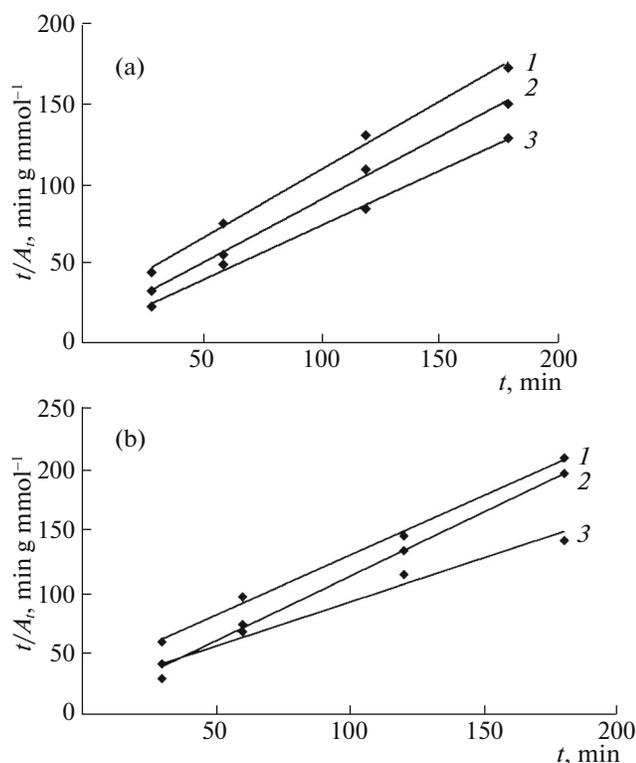
Fig. 4. Dependences of the relative values of the sorption capacity at moment t, according to experimental data on the sorption of (a) Co^{2+} and (b) Ni^{2+} ions by phytic sorbent. $T = $ (*1*) 20, (*2*) 40, (*3*) 60°C.

Linear dependences obtained from experimental data according to the equation of pseudo-second order are shown in Fig. 4.

The dependences shown in Fig. 4 indicate relative changes in the sorption capacity over time (t/A_t). The presented linear dependences are described with linear dependences. For Co^{2+} ions: $y = 0.8607x + 21.734$ (20°C), $y = 0.7943x + 9.3814$ (40°C), and $y = 0.6879x + 4.1827$ (60°C); for Ni^{2+} ions: $y = 0.961x + 31.281$ (20°C), $y = 1.0352x + 6.3932$ (40°C), and $y = 0.71x + 18.4$ (60°C). The constants for this chemical model were determined from the obtained linear equations (Table 2).

CONCLUSIONS

The effect of temperature on the kinetics of removal of Co^{2+} and Ni^{2+} ions by a sorbent based on an IHPA derivative fabricated from rice production waste (solid/liquid phase ratio S : L = 1 : 400; time, 1−180 min) was investigated. It was established that as the temperature rises from 20 to 60°C, we observe changes in the kinetics of removal of metal ions, and the sorption capacity of the phytic sorbent grows to 1.4 mmol g^{-1} for Co^{2+} ions and to 1.3 mmol g^{-1} for Ni^{2+} ions (the degree of removal for Co^{2+} ions was

92.1%; that for Ni^{2+} ions, to 81.0%). It was shown for the examined temperature range that order n of the sorption of Co^{2+} and Ni^{2+} ions is <1, which characterizes reactions accompanied by diffusion processes. It was established that the removal of Co^{2+} and Ni^{2+} ions is characterized by activation energies of 20.74 kJ mol^{-1} for Co^{2+} ions and 14.2 kJ mol^{-1} for Ni^{2+} ions, testifying to negligible changes in the reaction constant along with temperature changes. It was shown that the process of sorption in the analyzed time interval is best described by a kinetic model of pseudo-second order, as is indicated by the respective correlation coefficients. The obtained data can be used in selecting the optimum parameters of the removal of heavy metal ions using a sorbent based on an IHPA derivative and materials based on it.

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