STUDYING THE SORPTION OF PB^{2+} AND NI^{2+} IONS ON MODIFIED RICE HUSK BIOSORBENT

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Abstract: Modification of rice husks, considered as agricultural waste, in an aqueous solution of urea was carried out. Sorption of Pb^{2+} and Ni^{2+} ions on modified rice husk was studied in artificial solutions under static conditions. Factors affecting the sorption process, i.e. time, temperature, and concentration dependences were presented. From the results, the reaction order of the sorption process was calculated, and it was determined that the process is pseudo-second order. Langmuir and Freundlich isotherm constants of absorption of metal ions onto biosorbent were determined. According to the results, it was determined that the sorption corresponds to the Freundlich isotherm (solid-liquid environment).

Keywords: Biomass, biosorbent, modification, sorption, isotherm

Introduction

Biomass residues are considered sources of atmospheric pollution, causing environmental problems due to their low natural degradability and usually disposal by burning. They can be processed to obtain different types of materials. This also has a positive effect on the reduction of biomass waste. Researchers are using biomass and their modification products as adsorbents. Their use as biosorbents has been shown to be very promising compared to conventional treatment methods due to their low cost, high efficiency, easy recovery, and the ability to recover absorbed metal ions. The sorption properties of these materials are due to their natural pores and the functional group of the polymolecules in them [1,2]. They are widely used to soften the hardness of water in thermal and nuclear power plants, to desalinate water in water treatment facilities during production processes, and to separate ions of rare, precious, non-ferrous and heavy metals contained in technological solutions in hydrometallurgy.

Researchers studied the sorption properties of agricultural waste products and their modification products [3]. Rice husk also occupies a significant place among agricultural waste. Researchers have obtained various ion exchange substances by modifying rice husks and ash [4]. The article studied the dependence of Pb^{2+} and Ni^{2+} ions absorption of rice husk biosorbent modified by urea in aqueous solution on time, temperature and ion concentration. On this basis, the reaction order of sorption of metal ions to biosorbent, Langmuir and Freundlich isotherms, and thermodynamic correlation coefficients were calculated.

1. Experimental Methods

Preparation of solutions

Artificial solutions were prepared to study the sorption of metal ions to biosorbent. $Ni(NO_3)_2 \cdot 7H_2O$ "c" of Ni^{2+} ion and $Pb(CH_3COO)_2$ "c" salts of Pb^{2+} ion were used in this. The mass of salts needed to prepare 0.1 mol/L solutions was measured on an analytical balance. The resulting mass was dissolved in a small amount of distilled water, poured into a 1 L measuring flask and diluted.

1.2. Preparation of biomass

Rice husk biomass was harvested from the mill and mechanically processed. The resulting mass was left in a 3 % solution of alkali for 24 hours. Then it was washed in distilled water until pH=7. After washing, it was stored in an airtight container in distilled water for experiments.

1.3. Modification reaction

The hydroxyl group in alcohols displaces ammonia from urea [5]. Rice husk consists of cellulose, hemicellulose and lignin. Hydroxyl groups in them displace ammonia from urea at high temperature. The reaction equation can be written as follows (Figure 1).

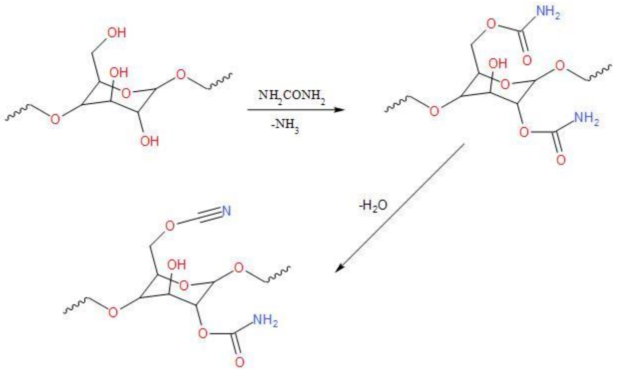

Fig. 1. Reaction equation for the modification of rice husk (biosorbent) with an aqueous solution of urea.

A biosorbent containing nitrogen was obtained by modifying rice husks in an aqueous solution of urea. The influence of various factors on the modification reaction was studied. For the modification reaction, 100 mL of 20 % urea solution was poured into 20 g of biomass and heated at 423 K for 4 hours.

2.4. Adsorption process

When studying the sorption of metal ions (Pb^{2+} and Ni^{2+}) from solutions, 0.1 of each metal ion; 0.075; 0.05; 0.025 mol/L solutions were prepared. In the sorption process, a biosorbent with a static exchange capacity of 6 mg-eq/g for hydrochloric acid was used. Adsorption processes were carried out at temperatures of 293, 303 and 313 K for 4, 8, 12, and 24 hours. The amount of absorbed ions was calculated from the difference in concentrations found in the UV-spectrophotometer of the initial and post-sorption solutions (1).

$$q_e = \frac{(C_0 - C_e)}{m} \times V \qquad (1)$$

here: q_e– the amount of metal ion absorbed into the biosorbent mol/g, C_0–the initial concentration of metal ions, mol/L, C_e–the equilibrium concentration of metal ions, mol/L; V–the solution volume, L; m–the sorbent mass, g [6-8].

2.5. Analysis of nitrogen content

2.5.1. Reagents for analysis

Concentrated sulfuric acid «c», perchloric acid (100 %) «c», Nessler's reagent «c» and Seignette's salt «c» were used to determination the amount of nitrogen in biomaterials by the Kjeldahl method.

2.5.2. Kjeldahl method

The amount of nitrogen, phosphorus and potassium (in %) in the plant can be determined by the Kjeldahl method [9]. After the biosorbent composition is modified, it will have the following composition (Figure 2).

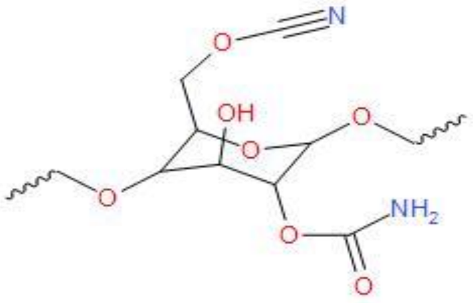

Fig. 2. Composition of biosorbent obtained by modification of rice husk with aqueous solution of urea. Determination of the amount of nitrogen in the biosorbent is carried out as follows. Initially, the biosorbent is rapidly burned in the presence of concentrated sulfuric and perchloric acids. Biosorbents can be decomposed under the influence of acid as follows. CnHmNx+H2SO4 → nCO2+m/2H2O+x/2(NH4)2SO4When conducting the experiment, first, 0.2-0.3 g of crushed biomass is placed in a conical flask with a capacity of 50-60 mL. 5 mL of concentrated sulfuric acid is poured over it and shaken, is tightly closed and left for 12–14 hours. Then the mixture is heated over low heat until white fumes of sulfuric acid appear. The flasks are removed from the heat and cooled, then 5–6 drops of perchloric acid are added, and boiled for another 5–7 minutes over high heat. If the solution does not discolouration, add another 1–2 drops of perchloric acid and continue boiling. 7–8 drops of perchloric acid are enough for complete discolouration of the mixture. The discoloured mixture is boiled for another 15 minutes over low heat. The flask is cooled and a small amount of distilled water is poured over it and transferred to a 100 mL volumetric flask. 10 mL of the solution is taken, and its volume is increased to 100 mL, and it is called "A" solution. 0.5-2.0 mL of the "A" solution is taken into a measuring flask with a capacity of 50 mL. Then 20-30 mL of water is poured into the flask and neutralized with 10 % NaOH solution until the light pink colour of the solution disappears in the presence of 1 drop of methyl red. 2 mL of a 50 % solution of Seignette's salt and 2 mL of Nessler's reagent are poured over it. The

concentration of nitrogen in the solution is determined in a UV-spectrophotometer.

The amount of nitrogen is determined based on the calibration curve. For this, 0.7405 g of ammonium chloride is taken and dissolved in 1000 mL of water. 10 mL is taken from it and the volume is brought to 500 mL. To prepare the calibration curve, 5, 10, 15, 20 and 25 mL are taken, and the above-mentioned reagents are added to it. The concentration of nitrogen in solutions is also determined in a UV-spectrophotometer. The light refractive index of solutions is determined in a UV-spectrophotometer.

3. Theoretical part

3.1. Sorption kinetics

Pseudo-first order, pseudo-second order and several other methods are used to study the reaction order of the adsorption process [10-12]. Kinetic models are used to determine the mechanism of the sorption process. That is, these models allow for obtaining important information about the rate of chemical reaction, diffusion process and mass exchange. The following kinetic models were used in the study.

3.1.1. Pseudo-First-Order Kinetic Model

It is represented by equation (2) below.

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2,303}t \qquad (2)$$

In this equation: q_t and q_e are the amount of sorbent metals at a certain time and equilibrium (mg/g). k_1 is the speed of the first-order sorption process (min^{-1}), and the angular value of the intersection slope in the linear graph of the log (q_e-q_t) and time t is k_1/2,303 [13].

3.1.2. Pseudo-Second-Order Kinetic Model

It is represented by equation (3) below.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + (\frac{1}{q_e})t \qquad (3)$$

The initial sorption rate (t = 0) is found as follows (4).

$$h = k_2 q_e^2 \qquad (4)$$

In this equation: k_2– the velocity constant, q_e – the amount of metal absorbed in a sorbent of the certain mass (mg/g), t-time (minutes) [14].

3.2. Study of adsorption equilibrium

Adsorption isotherms are the most important tool for the analysis of equilibrium processes. Of the many models used to represent equilibrium processes in liquid-solid systems, the most widely used and convenient are the Langmuir and Freundlich models [15].

3.2.1. Langmuir isotherm model

It is represented by thef following equation (5):

$$q_e = q_{\max} \frac{K_L C_e}{1 + K_L C_e} \qquad (5)$$

here: q_e - the amount of metal ion absorbed into the ion exchanger mol/g, C_e - the equilibrium concentration of the solution (mol/g), q_{max} – the maximum amount of metal absorbed in a sorbent of a certain mass (mol/g). In order to find the Langmuir constant (K_L), a linear form of Langmuir's equation (5) is used, where the values of q_{max} and K_L are determined from the C_e dependence graph of C_e/q_e (6).

$$\frac{C_e}{q_e} = \frac{1}{q_e K_L} + \frac{1}{q_{\max}} \times C_e \qquad (6)$$

An important feature of the Langmuir isotherm parameters is that the separation coefficient "R_L" can be used to draw conclusions about the relationship between the adsorbent and the adsorbate.

$$R_L = \frac{1}{1 + K_L C_0} \qquad (7)$$

In this case, according to (4), the adsorption process $0<R_L<1$ is comfortable, $R_L>1$ is uncomfortable, $R_L=1$ is linear, and $R_L=0$ is irreversible [16].

3.2.2. Freundlich isothermal model

It is represented by the following equation (8)

$$q_e = K_F C_e^{1/n} \qquad (8)$$

By using the Freundlich isotherm equation, it is possible to study sorption processes occurring in various (non-ideal) solutions. The linear equation of this model can be expressed as follows (9).

$$\log q_e = \log K_F + (\frac{1}{n}) \log C_e \qquad (9)$$

In this (9) equation: q_e – the amount of metal absorbed into the sorbent of a certain mass (mg/g), K_F- The Freundlich constant, C_e- the equilibrium concentration of the solution (mg/L), 1/n – the sorption intensity. The values K_F and n (n≈1–10) of the Freundlich constant are found by the angular value of the slope of the intersection on the linear graph of $\log q_e$ with $\log q_t$ [12-16].

3.3. Thermodynamic analysis

In this study, the adsorption process at 293, 303, and 313 K temperatures was studied. it is possible to calculate the change in free energy of the process (10)

$$\Delta G^0 = -RT \ln K_e \qquad (10)$$

In the linear graph of $\ln K_e$ and 1/T, the values (11) of ΔH° and ΔS°are found by the angular value of the intersection slope [17].

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \qquad (11)$$

4. Results and Discussion

4.1 Adsorption capacity

A number of researchers have carried out modification reactions of cellulose-containing waste biomass with various substances. They determined the sorption of metal ions to the obtained biosorbent [3, 18-20]. In the study, it was found that the biosorbent obtained from the modification of rice husk with an aqueous solution of urea adsorbs Pb^{2+} ion 354.9 mg/g, and Ni^{2+} ion 268.35 mg/g. We can see that the biosorbent is competitive with other types of sorbents in the amount of absorption of metal ions. In addition, rice husk is a significant part of domestic waste in many countries. Reuse of this biomass reduces their accumulation.

4.2. Kinetic results

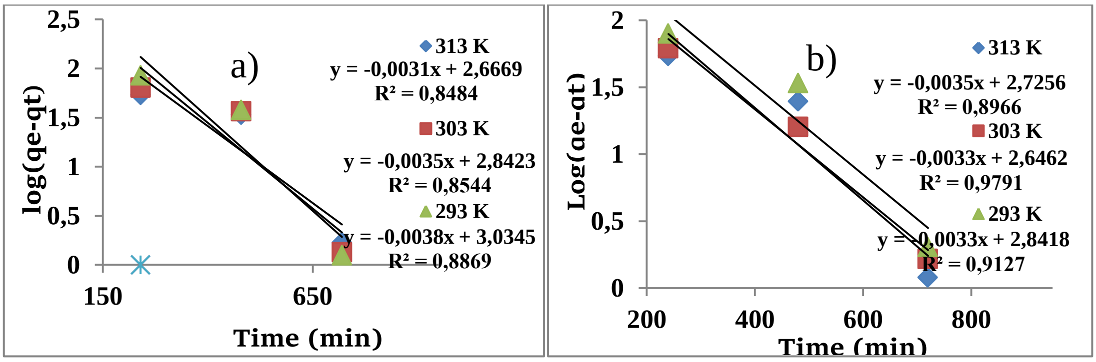

Fig. 3. Pseudo-First kinetic model of absorption of a-Pb^{2+} and b-Ni^{2+} ions into biosorbent.

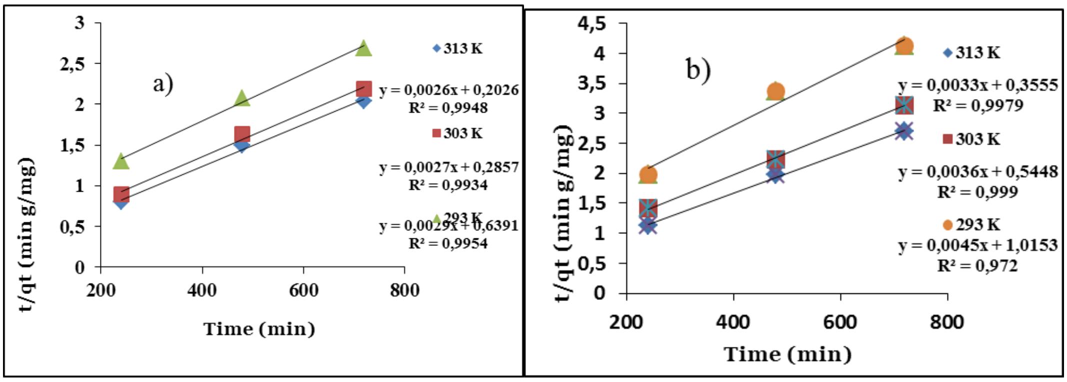

Fig. 4. Pseudo-Second-Order kinetic model of absorption of a-Pb^{2+} and b-Ni^{2+} ions into biosorbent.

Using the graph, the constant values of the kinetic models were calculated (Table 1, 2).

Table 1. Pseudo-first order constants of Pb^{2+} and Ni^{2+} ions found at different temperatures.

Metal ion.	T, K	K, min^{-1}	R^2
	293	-0.000158	0.880
Pb^{2+}	303	-0.000146	0.850
	313	-0.000129	0.848
Metal ion.	T, K	K, min^{-1}	R^2
	293	-0.000138	0.910
Ni^{2+}	303	-0.000113	0.980
	313	-0.000146	0.890

Table 2. Pseudo-second order constants of Pb^{2+} and Ni^{2+} ions found at different temperatures.

Metal ion.	K, min^{-1}	q_e	R^2
	0.000033	384	0.990
Pb^{2+}	0.000025	370	0.990
	0.000013	344	0.999
Metal ion.	K, min^{-1}	q_e	R^2
	0.00002	222	0.990
Ni^{2+}	0.000024	277	0.990
	0.000031	303	0.990

From the kinetic constants in Tables 1, and 2 above, we can see that the sorption of metal ions to the biosorbent corresponds to the pseudo-second-order kinetic model. That is, it means that the sorption process takes place at the expense of the functional group of the biosorbent and the mobility of the ions.

4.3. Sorption isotherm

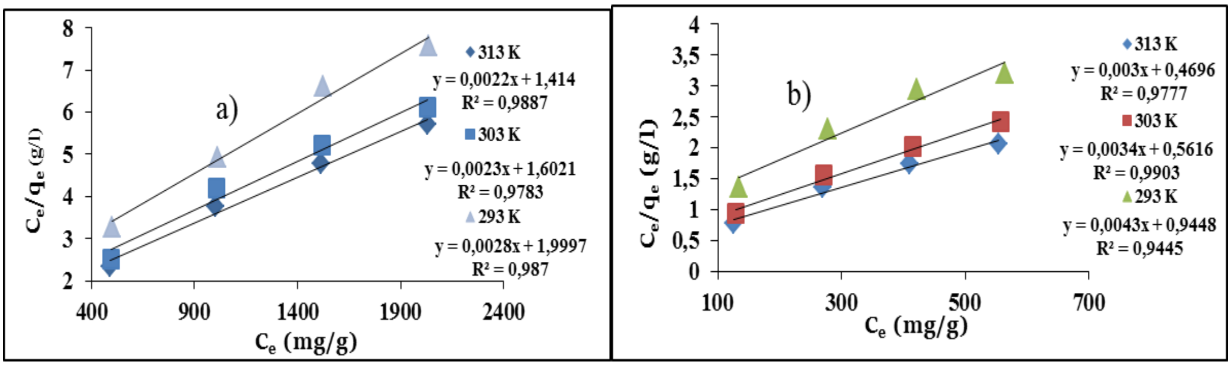

Fig. 5. Langmuir isotherm of adsorption of a-Pb^{2+} and b-Ni^{2+} ions to biosorbent.

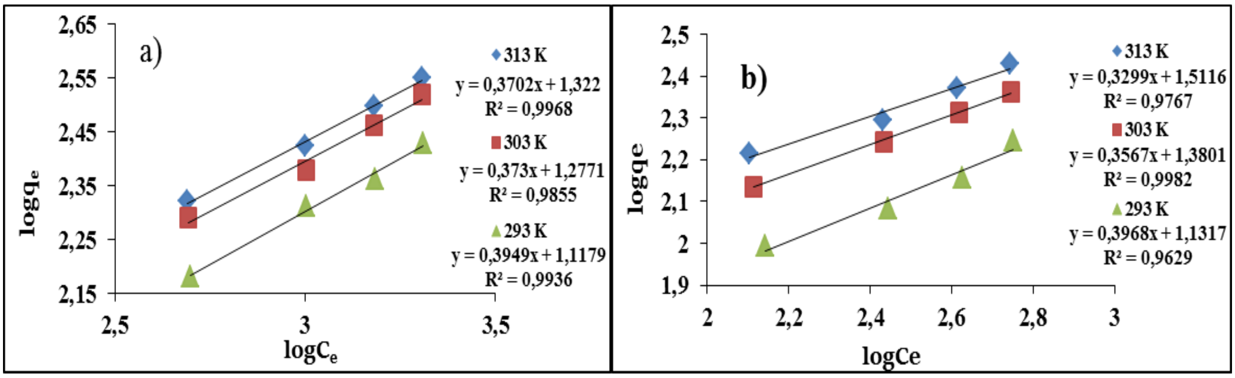

Fig. 6. Freundlich isotherm of adsorption of a-Pb^{2+} and b-Ni^{2+} ions to biosorbent.

Langmuir and Freundlich isotherms and thermodynamic values were calculated for Pb^{2+} and Ni^{2+} ions (Table 3, 4).

Table 3. Freundlich isotherm constants of Pb^{2+} and Ni^{2+} ions found at different temperatures.

Metal ion.	T, K	K_F, L mg^{-1}	R^2
	293	13.11	0,990
Pb^{2+}	303	18.92	0,990
	313	20.98	0,990
Metal ion.	T, K	K_F, L mg^{-1}	R^2
	293	13.54	0,970
Ni^{2+}	303	23.99	0,990
	313	32.48	0,960

Table 4. Langmuir isotherm constants of Pb^{2+} and Ni^{2+} ions found at different temperatures.

Metal ion.	T, K	K_L, L mg^{-1}	R_L	R^2
	293	0.276	0.147	0.930
Pb^{2+}	303	0.297	0.173	0.978
	313	0.322	0.18	0.980
Metal ion.	T, K	K_L, L mg^{-1}	R_L	R^2
	293	0.238	0.283	0.930
Ni^{2+}	303	0.355	0.333	0.990
	313	0.375	0.362	0.977

Tables 3 and 4 show the correlation values of Langmuir and Freundlich equation sorption isotherms. The R_L values of Pb^{2+} (0.147; 0.173; 0.18) and Ni^{2+} (0.283; 0.333; 0.362) ions in the Langmuir isotherm indicate that sorption is favourable. The Freundlich parameter (n) values were n=2.53, 2.68, 2.7 and n= 2.52, 2.8, 3.03 for Pb^{2+} and Ni^{2+} ions, respectively. This indicates that the sorption of metal ions to the biosorbent is at a high level. The values of correlation coefficients R^2 were equal to Pb^{2+} (0.99; 0.99; 0.99) and Ni^{2+} (0.97; 0.99; 0.96). Correlation values (R^2) indicate that the adsorption process obeys the theory of Freundlich adsorption.

4.4. Thermodynamic analyses

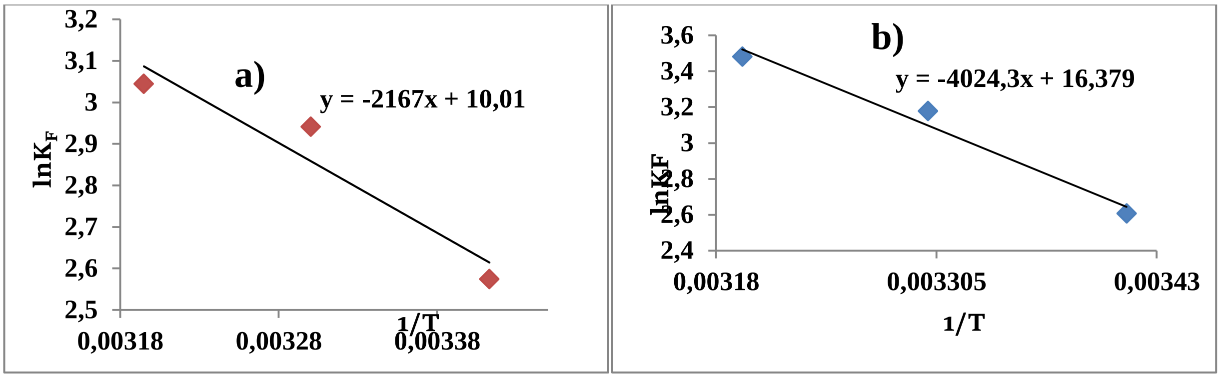

Fig. 7. Thermodynamics of adsorption of a-Pb^{2+} and b-Ni^{2+} ions onto biosorbent.

Changes in thermodynamic parameters during the sorption processes of Pb^{2+} and Ni^{2+} ions from solutions in the temperature range of 293, 303 and 313 K to biosorbent were calculated (Table 5).

Table 5. Changes in adsorption equilibrium constants and thermodynamic functions of Pb^{2+} and Ni^{2+} ions to biosorbent.

Metal ions	, K	K_F, L/mol	$-\Delta G^0$, kJ/mol	$-\Delta H^0$, kJ/mol	ΔS^0 kJ/mol·K
Pb^{2+}	293	13.12	6.2706	18.017	83.22
	303	18.93	7.40776		
	313	20.99	7.92135		

Metal ions	, K	K_F, L/mol	$-\Delta G^0$ kJ/mol	$-\Delta H^0$ kJ/mol	ΔS^0 kJ/mol·K
Ni^{2+}	93	13.54	6.347	33.46	136.17
	03	23.99	8		
	13	32.48	9.06		

ΔH_0 given in the table has a negative value. This means that the adsorption process is exothermic. The decrease in free energy indicates that the absorption of Pb^{2+} and Ni^{2+} ions on biosorbents is spontaneous.

Conclusions

The sorption of Pb^{2+} and Ni^{2+} ions on the sorbent obtained from the modification of agricultural waste rice husk in an aqueous solution of urea was studied. Sorption processes were carried out in artificial solutions under static conditions. Factors affecting the sorption process, i.e. dependence on time, temperature and concentration were studied. The reaction procedures of metal ion sorption were studied. The sorption process was found to be pseudo-second order. That is, the mobility of metal ions and functional groups in the sorbent were involved in the sorption process. In this case, the unshared electron pairs of the nitrogen atom in the biosorbent are combined with the metal ions, forming a mutual donor-acceptor bond. Absorption isotherms of metal ions on biosorbent were calculated at different temperatures. Based on the results, absorption was determined to be compatible with solid-liquid adsorption (Friendlich isotherm). Thermodynamic parameters of the sorption process, isothermal-isobaric potentials, changes in free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) values were calculated in the study. It means that the process of free energy reduction in the sorption process proceeds by itself.

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