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Research paper

Material Performance of Nickel Ions Adsorption by Larix Sibirica Needles

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Abstract

Adsorption of ions of nickel on alternative sorption material - needles of Siberian larch *(Larix sibirica)* is investigated at temperatures of 20, 30 and 40 ^{0}C. The maximum sorption capacities of needles *of Larix sibirica* in relation to ions of nickel (II) at temperatures of 20 are determined °C, 30° C, 40° C which made 0,80 mmol/g (47,2 mg/g), 0,87 mmol/g (51,3 mg/g) and 0,92 mmol/g (54,3 mg/g) respectively. Isotherms of adsorption are received and shortchanged with use of models of Langmuir, Friendlich, Temkin and Dubinin-Radushkevich. It is defined that process of adsorption of ions of Ni^{2+} at a temperature of 20the ° C is best of all described by Friendlich's model (R2 = 0,983), and at temperatures of 30° C and 40° C - the Langmuir model (R2 = 0,995 and 0,996 respectively). By the carried-out calculations it is defined that process of adsorption of ions of Ni^{2+} needles *of Larix sibirica* treat processes of physical adsorption as values of energy of adsorption have size less than 8 kJ/mol, and values of energy of Gibbs demonstrate spontaneous course of physical adsorption. Processing of kinetic dependences of processes of adsorption of ions of nickel (II) *Larix sibirica* needles at three temperatures within diffusive model defined the limiting stages of processes - the mixed diffusion.

Keywords: ***:*** *sorption material, needles of a larch Siberian, ions of nickel, adsorption isotherm, water purification.*

1. Introduction

In the field of cleaning natural and sewage the new innovative direction - use as reagents of waste of industrial and agricultural production and natural mineral environments appeared now. Use of the called reagents is especially relevant for removal from water environments of the ions of heavy metals (IHM). The last, as a rule, are present at water objects in the dissolved state that does the majority of physical and chemical ways of cleaning inefficient, and use of reagent chemical cleaning, especially in natural reservoirs, impossible. Use of sorption technologies can be an exit from the situation. Application of traditional sorbents - absorbent carbon is limited to their high cost and low sorption capacity in relation to many ITM.

Due to the above, as sorption materials renewable cellulose containing waste from processing of agricultural raw materials is of special interest for extraction of ITM [1-10]. The separate position in a case in point is made by waste from processing of wood biomass (sawdust, shavings, and spill) and components of trees (leaves, fruits, needles, cones, etc.). It is shown that sawdust of wood [11-15] and bark [16, 17], leaves [18, 19], the crushed fruits [20, 21], seeds of fruits [22], cones [23] effectively delete ITM from water solutions.

Leaves and needles of trees of various types are of special interest. Advantage of foliage is that the last have big annually renewable biomass, and needles - big in comparison in foliage the area in terms of unit of mass. Use of needles of trees of coniferous types as sorption materials for extraction of pollutant including ITM, is shown, in particular, in works [24-26]. The needles of trees *of the type Larix* are of special interest in view of the fact that they as well as trees of sheet types in the conditions of the Russian Federation dump needles before the winter period.

On the basis of the above, sorption of ions of Ni (II) with use as sorption material of needles of Siberian larch *(Larix sibirica)* was investigated. In the world literature there are messages about a research of sorption of ions Cr(III) and Cr(VI) needles of larch pre-Jurassic *Lárix gmélinii [27]* and thin-scaled larch *(Larix leptolepis)* [28].

2. Methods

In experiments the dry fallen-down needles of a season of 2016 were used. Originally determined the sizes of the studied sorption material. For this purpose 100 needles were randomly selected and by means of a ruler and a micrometer their length and thickness were measured. By the taken measurements and the corresponding mathematical calculations it is defined that needles have average value of length of 30,5 mm, thickness - 560 microns. Further some physical parameters specified in table 1 were defined.

In the subsequent isotherms of sorption of ions of Ni were under construction^{2+} needles *of Larix sibirica* (table 1) at temperatures of 20 0C, 30 0C and 40 0C. For this purpose in flat-bottomed flasks of 250 cm^3 hinge plates of sorption materials on 1 g were located with weight. Then in flasks about 100 cm were filled in^3 solutions containing Ni ions^{2+} in concentration of 10-1500 mg/dm^3.

Table 1:. Physical properties of Larix sibirica needles.

Property	Value
Bulk density ρ, g/cm^3	0,06
Moisture W, %	11,25
Ash content A_c, %	0,50
Buoyancy P, %	56,44

As the connections containing Ni ions in the structure^{2+}, for preparation of model solutions $NiSO_4 \cdot 7H_2O$ were used. Hinge plates of sulfate of nickel undertook taking into account crystallizational water. Flasks with the hinge plates and the corresponding solutions which are in them were densely closed by traffic jams and vigorously stirred up within 5 hours. Then needles were filtered and in filtrates equilibrium concentration of ions of Ni (II) were defined by a photometric method [28].

On the basis of the obtained experimental data, the sorption capacity of needles of a larch (A) on a formula is calculated:

And = ($_{Cs}$ - $_{Se}$) • V/m (1)

where And - sorption capacity on ITM (mmol/g), $_{Cs}$ - initial concentration of ITM (mmol/dm3), $_{Se}$ - concentration of ITM after sorption (mmol/dm3),

V - solution volume (dm3), m - weight sorption swore ().

3. Results and Discussion

Isotherms of sorption of ions of Ni^{2+} on *Larix sibirica* needles at various temperatures are presented in the figure 1.

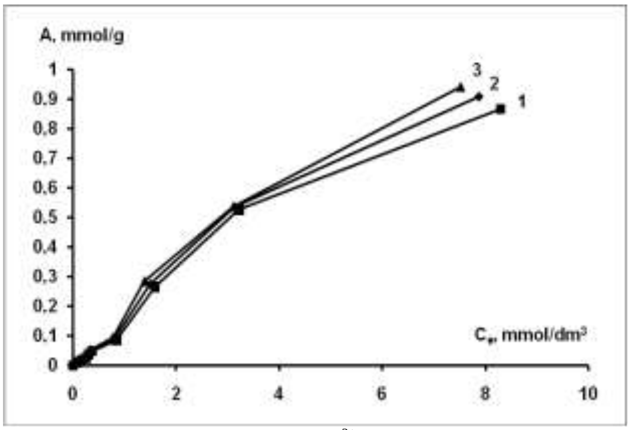

Fig. 1:. Isotherms for adsorption of Ni^{2+} *ions by Larix sibirica needles at different temperatures*: 1 - 20 ° C, 2 - 30 ° C, 3 - 40 ° C.

According to the figure 1 it is visible that the received isotherms belong to isotherms of the I type of classification of BDDT or the L type according to Gils's classification and describe monomolecular adsorption of ions of Ni^{2+} on needles of a larch [29]. The maximum sorption capacities of needles *of Larix sibirica* in relation to ions of nickel (II) at temperatures of 20 are determined° C, 30° C, 40° C which made 0,80 mmol/g (47,2 mg/g), 0,87 mmol/g (51,3 mg/g) and 0,92 mmol/g (54,3 mg/g) respectively.

Due to the aforesaid, with a research objective of course of mechanisms of processes of adsorption, the received isotherms are processed within four monomolecular models of adsorption: Langmuir, Friendlich, Dubinin-Radushkevich and Temkin [29], according to the equations:

Langmuir $$\frac{1}{A} = \frac{1}{A_\infty} + \frac{1}{K_L \cdot A_\infty \cdot C_e}$$

Friendlich logA = $_{\text{logKF}}$ + $_{\text{n logCe}}$

Dubinina-Radushkevich $$\ln A = \ln A_\infty - \left(\frac{R \cdot T}{E}\right)^2 \cdot \left(\ln \frac{C_s}{C_e}\right)^2$$

Temkina $$A = \frac{R \cdot T}{b_{TE}} \cdot \ln a_{TE} + \frac{R \cdot T}{b_{TE}} \cdot \ln C_e$$

As criterion of compliance the approximation coefficient was used (R2), which value equal 1, means that full compliance of process of this model of sorption is observed; the value of coefficient of approximation is closer to unit, the better this model describes the studied process.

Results of processing of isotherms of adsorption of ions of nickel (II) *Larix sibirica* needles at temperatures of 20° C, 30° C, 40° C within monomolecular models: Langmuir, Friendlich, Dubinin-Radushkevich, Temkin are presented in table 2.

Table 2:. Mathematical treatment of isotherms for adsorption of Ni^{2+} *ions by Larix sibirica needles.*

Adsorption model	Temperature		
	20ºC	30ºC	40ºC
Langmuir	y = 6,785x + 3,520 R^2 = 0,975	**y = 7,437x + 0,315** **R^2 = 0,995**	**y = 6,882x + 0,043** **R^2 = 0,996**
Freindlich	**y = 1,001x - 0,898** **R^2 = 0,983**	y = 1,016x - 0,859 R^2 = 0,987	y = 1,009x - 0,825 R^2 = 0,988
Dubinin-Radushkevich	y = -3E-08x - 0,653 R^2 = 0,936	y = -3E-08x - 0,654 R^2 = 0,930	y = -3E-08x - 0,638 R^2 = 0,929
Temkin	y = 0,176x - 0,420 R^2 = 0,816	y = 0,185x - 0,438 R^2 = 0,825	y = 0,190x - 0,440 R^2 = 0,825

According to table 2 follows that at increase in temperature distribution of the active centers with identical values of sorption energy on the surface of material becomes more uniform that is caused by increase in coefficients of approximation of the Langmuir model.

Thermodynamic constants: sorption energy (E), Gibbs's (ΔG) energy, enthalpy (ΔH) and entropy (ΔS) of processes of sorption of ions of Ni^{2+} *Larix sibirica* needles at temperatures of 20 ° C, 30 ° C, 40 ° C are calculated for the purpose of definition of the nature of processes of sorption (physical or chemical) on formulas 3-6 [29] and presented in table 3.

ΔG = - R • T • $_{\text{lnKL}}$,
(3)
E = $(-2\beta)^{-1/2}$,
(4)
ΔH = R • (T2-T1) / ($_{T2}$ • $_{T1}$) • ln (KL2/KL1),
(5)
ΔS = (ΔH - ΔG) / T,
(6)
where β - Dubinin-Radushkevich's constant.

Table 3:. Thermodynamical constants of adsorption processes of Ni^{2+} *ions by Larix sibirica needles.*

Temperature, ºC	E, kJ/mol	ΔG, kJ/mol	ΔH, kJ/mol	ΔS, J/(mol · K)
20	4,082	-1,626	8,023	32,93
30	4,082	-7,832		
40	4,082	-12,575		

According to table 3 it is visible that processes of adsorption of ions of Ni^{2+} *Larix sibirica* needles at all three temperatures treat processes of physical adsorption as values of energy of adsorption less than 8 kJ/mol and values of an enthalpy less than 100 kJ/mol, and values of energy of Gibbs in the range from-20 to 0 kJ/mol speak about spontaneous course of physical adsorption [29].

At the following stage the kinetics of processes of adsorption of ions of nickel (II) *by Larix sibirica* needles on model solutions of 0,1 dm is studied^3, with initial concentration of ions of nickel (II) of 1000 mg/dm^3, time of sorption from 0 to 180 min. and dosage of sorption material of 1 g. Kinetic dependences of processes of sorption of ions of nickel (II) are constructed *by Larix sibirica* needles at temperatures of 20 ° C, 30 ° C, 40 ° C (figure 2).

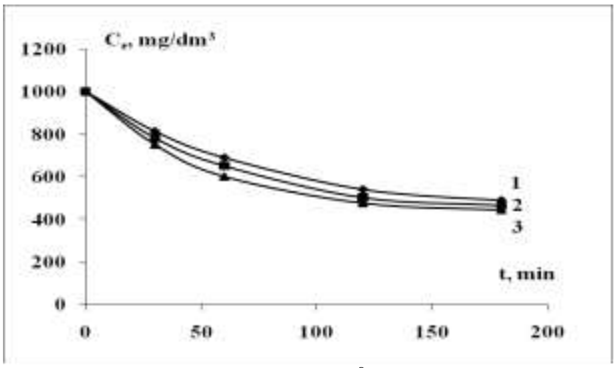

Fig. 2:. Kinetic curves for adsorption of Ni^{2+} *ions by Larix sibirica needles at different temperatures*: 1 - 20 ° C, 2 - 30 ° C, 3 - 40 ° C.

As a rule, processes of physical adsorption are described with use of diffusive model which considers a contribution external (formula 7) and internal diffusion (formula 8) in adsorption process course. Biot's criterion calculated by a formula 9 in the range from 0 to 1 indicates that the limiting stage of process of adsorption is external diffusion, that is process of diffusion of an adsorbate in solution to the surface of adsorbent, at values of coefficient of Biot more than 20 the stage of internal diffusion, that is diffusion of an adsorbate in an adsorbent time is limiting, and at values of coefficient of Biot from 1 to 20 - the mixed diffusion, that is in process of adsorption makes an identical contribution both process external, and process of internal diffusion.

$$D_{вн} = \frac{r_0 \cdot \delta \cdot \gamma \cdot A}{3 \cdot Ce},$$

(7)

$D_i = B_t \cdot r2 / (\pi^2 \cdot t),$

(8)

$$Bi = \frac{D_{вн} \cdot r}{D_i \cdot \delta \cdot K_p},$$

(9)

where D_{vn} - coefficient of external diffusion, r_0 - the radius of particles of a sorbent (cm),
δ - solution film thickness around granules of a sorbent (cm), γ - some size, a constant for these conditions, A - the sorption capacity (mmol/g), S_e - equilibrium concentration of sorbate in solution (mmol/cm3),
D_i - coefficient of internal diffusion (cm2/c), B_t - criterion of a homochromousness of Fourier, *r* - the radius of grain of a sorbent (cm), *t* - time (c), B_i - Biot's coefficient,
K_p - the distribution coefficient determined by the equation: K_p = And / C_e.
Kinetic dependences of processes of adsorption of ions of nickel (II) at three temperatures are processed *by Larix sibirica* needles within diffusive model of adsorption, Biot's coefficients presented in table 4 are calculated.

Table 4:. Values of Bio ratio for adsorption of Ni^{2+} *ions by Larix sibirica needles at different temperatures.*

Temperature	Time, min				
	0	30	60	120	180
20 ºC	-	8,91	6,57	1,83	-
30 ºC	-	8,89	6,37	1,74	-
40 ºC	-	7,84	5,29	1,70	-

Values of coefficients of Biot in all period in the range from 1 to 20 indicate that the limiting stage of processes is the mixed diffusion.

4. Summary

Mathematical processing of isotherms of adsorption of ions of nickel (II) needles of a larch of the Siberian *Larix sibirica* with use of various models showed that process of adsorption of ions at a temperature of 20 the ° C is best of all described by Friendlich's model (R2 = 0,983), and at temperatures of 30 ° C and 40 ° C - the Langmuir model (R2 = 0,995 and 0,996 respectively). Values of sorption energy (~ 4 kJ/mol) and Gibbs's energy (from-12,6 to-1,6 kJ/mol) on the basis of which process of sorption of ions of Ni are calculated^{2+} at all three temperatures are carried to processes of physical adsorption, proceeding spontaneously. By a research of kinetics of processes of adsorption of ions of nickel (II) at three temperatures within diffusive model it is revealed that the limiting stage of processes is the mixed diffusion.

5. Conclusions

Thus, the possibility of use of Ni (II), dried up biomass of needles of a larch Siberian for sorption extraction of ions, from model solutions is shown by the made experiments. Isotherms of adsorption of the called ions on needles *of Larix sibirica* are constructed and shortchanging with use of models of Langmuir, Freundlich, Dubinin-Radushkevich and Temkin is made. The calculated values of thermodynamic parameters of adsorption of ions Ni(II) from water solutions at various temperatures allow referring this process to physical adsorption.

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