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Physical and Chemical Regularities of Phosphorus and Beryllium Recovery by the Sorbents Based on Acrylic Fiber Impregnated by Iron Hydroxide (III)

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Abstract: The paper investigates the physicochemical regularities (kinetics and isotherm) of phosphorus and beryllium recovery by sorbents based on polyacrylonitrile (PAN) fiber and Fe(OH)₃ obtained by various methods: PAN or pre-hydrolyzed PAN with precipitation of FeCl₃ with ammonia, using ready-made or electrochemically generated Na₂FeO₄, pre-hydrolyzed PAN treated with an alkaline solution of Na₂FeO₄, as well as their comparison with granular aluminum oxide. The Langmuir, Freundlich and Dubinin–Radushkevich models show high performance of materials for sorption of stable P and Be used as tracers for the release of ⁷Be, ³²P, and ³³P from seawater. The obtained kinetic data are processed using kinetic models of intraparticle diffusion and the pseudo-first-order, pseudo-second-order, and Elovich models. Optimal conditions for obtaining sorbents are established, namely, the effect of NaOH concentration at the stages of preparation on the properties of sorbents based on the PAN fiber and Fe(OH)₃ obtained by various methods.

Keywords: sorption; marine radiochemistry; Fe(OH)₃ fiber; aluminum oxide; kinetics; isotherm; phosphorus; beryllium



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1. Introduction

Regarding the sorption concentration of ⁷Be from seawater, V.B. Silker proposed the first method for recovering ⁷Be from seawater by granular aluminum oxide [1]. This method has many advantages. Aluminum oxide is an inexpensive and widely available material used for gas purification in industrial plants and other areas. It is possible to measure the adsorbers directly in Marinelli's vessels by γ -spectrometry. The recovery rates of ⁷Be at high rates of sample filtration (about 10 column volumes/min) are low, less than 60%, but this makes it possible to reliably determine the activity on the second adsorber and the sorption efficiency. When using samples with a volume of 2–8 m³, it is possible to measure the activity even with the use of scintillation γ -spectrometers. This method is successfully used at present, and the obtained data have allowed the construction of a mathematical model of the distribution of ⁷Be in the surface layer of the Black Sea [2,3].

At the same time, polypropylene cartridges [4] or acrylate fiber [5] impregnated with Fe(OH)₃ are widely used in foreign studies to extract ⁷Be from seawater. Some researchers [5,6] use seawater samples with a volume of 0.5–1 m³ with the addition of a stable isotope as a sorption efficiency tracer. Then, the fiber is ashed, and the ash is placed in a certain geometry for measurement by γ -spectrometry. After radiochemical preparation, the load can be used to determine the activity of ³²P, and ³³P [4]. The method

currently used in [5,6] is the most efficient for ^7Be scavenging since the sorption efficiency is more accurately determined from the stable beryllium with no need to measure the second sorbent, often showing a high error value. Sorption efficiency values are obtained by measuring seawater samples by spectrometry methods. However, small sample volumes require low-background gamma spectrometers. The disadvantage of this method is the use of a large amount of fiber—200 g per sample.

Sorption concentrations of ^{32}P , and ^{33}P from seawater.

Nutrient deficiency in seawater occurs due to their consumption by marine microorganisms [6]. In this case, the biological productivity of the ecosystem is set by the element with the greatest deficiency. Most often, the nutrient that determines the rate of formation of primary production is phosphorus [7]. Short-lived cosmogenic phosphorus isotopes make it possible to obtain the values of phosphorus biodynamics indicators in the marine environment [8].

There are two main approaches to this issue. The first is the standard method by which metabolism is studied in biology [9]. Seawater containing microorganisms is sampled, a radiotracer (most often ^{32}P) is poured into the seawater, and then, after a set time, the seawater is filtered to remove ^{32}P -absorbing microorganisms, and the residual activity of ^{32}P is determined. This method has a significant advantage—a large number of samples can be processed since the activities are easily measured by most models of β -radiometers. In addition, it does not require a time-consuming procedure for radiochemical sample preparation. The main disadvantage is the complex organization of work (production, purchase, delivery) with a short-lived isotope that loses 5% of its activity per day. Until recently, the production of ^{32}P in Russia was interrupted. This method was successfully developed in the USSR by the eminent oceanologist Yu. I. Sorokin [10].

The second approach was proposed by D. Lal, a pioneer in the study of cosmogenic radionuclides [11,12]. This method is based on scavenging ^{32}P and ^{33}P from seawater with fiber impregnated with $\text{Fe}(\text{OH})_3$. $\text{Fe}(\text{OH})_3$ was successfully used in the study of rainwater for the coprecipitation of radionuclides as a collector [13]. The disadvantages of this method are: it is necessary to process samples of large volumes (up to 10 m^3), to conduct radiochemical sample preparation quickly, and to use ultra-low-background instruments. Due to these difficulties, the number of works in this area is rather limited. C. Benitez-Nelson from Woods Hole Oceanographic Institute developed D. Lal's methods in her works [14]. C. Benitez-Nelson was the first to propose the use of polypropylene cartridges on the based $\text{Fe}(\text{OH})_3$ to extract ^{32}P and ^{33}P from seawater [15]. This technique was also used in [4]. These cartridges extract phosphorus from seawater more efficiently than fiber, but their hydrodynamic stability is higher. Using two adsorbers to obtain recovery data requires expensive pumping equipment. In addition, this value will contain the methodological error associated with $\text{Fe}(\text{OH})_3$ washout from the support. The use of one adsorber with the addition of a natural isotope to determine the degree of recovery requires large total volume containers on the vessel to build a detailed profile. We used containers with a total volume of 8 m^3 for recovery of ^{32}P and ^{33}P from seawater by a one-column method with the addition of stable phosphorus as an efficiency indicator. Two samples with a volume of 3 m^3 each were taken from the lower horizons; a sample with the highest activity of 2 m^3 was taken from the surface [16].

We should mention a promising method of preparation of sorbents with chemically fixed $\text{Fe}(\text{OH})_3$ on the surface of a support, for example, cellulose [17]. For this purpose, the acrylic fiber is oxidized with Na_2FeO_4 , which is produced electrolytically. This fiber, in which hydrated iron oxides are chemically bonded to the carrier, has shown to be more efficient than that obtained by the precipitation of $\text{Fe}(\text{OH})_3$.

In the above works, the study of the physicochemical laws of sorption was not carried out; however, such a study is important for understanding the course of sorption processes and makes it possible to select the optimal conditions for the quantitative recovery of the radionuclide and a stable tracer. In our previous work [18], we carried out a comparative

study of the methods for obtaining fibrous sorbents impregnated with $\text{Fe}(\text{OH})_3$ and their sorption characteristics in laboratory and field conditions.

This work aims to study the physicochemical regularities (kinetics and sorption isotherms) of the sorption of stable phosphorus and beryllium, which are widely used as tracers of the sorption efficiency of such radionuclides as ^7Be , ^{32}P , and ^{33}P from seawater.

2. Materials and Methods

The methods and materials for obtaining sorbents were described earlier in [18]. Sorbents obtained by various methods were named as follows: using non-hydrolyzed PAN and precipitation of $\text{Fe}(\text{OH})_3$ with ammonia—Fe-NH (non-hydrolyzed) [19]; obtained using electrochemically generated Na_2FeO_4 —Fe-EGSF (electrochemically generated sodium ferrate); ready-made Na_2FeO_4 —Fe-SF (sodium ferrate); pre-hydrolyzed PAN with precipitation of $\text{Fe}(\text{OH})_3$ with ammonia—Fe-H (hydrolyzed) [20].

2.1. Determining the Sorption Parameters of Phosphorus and Beryllium under Static Conditions

The determination of sorption parameters under static conditions was carried out by extracting phosphorus and beryllium by the obtained sorbents from seawater with the addition of stable phosphorus and beryllium to concentrations of 0.1 and 0.3 mg/L, respectively, for 48 h. Each experiment was repeated several times (three series of three experiments for each time point).

The concentration of phosphorus and beryllium in solutions was determined on a KFK-3-01 photometer (Zagorsk Optical and Mechanical Plant, Sergiev Posad, Russia).

The sorption efficiency (R , %), sorbent capacity (q , mg/g), and distribution coefficient (K_d , mL/g) were determined as described in [18].

2.2. Sorption Kinetics of Stable Isotopes of Phosphorus and Beryllium

The sorption kinetics was studied by recovering phosphorus and beryllium with the obtained sorbents from seawater with the addition of stable phosphorus and beryllium to concentrations of 0.1 and 0.3 mg/L, respectively, for various times. Each experiment was repeated several times (three series of three experiments for each time point).

2.3. Sorption Isotherm of Stable Isotopes of Phosphorus and Beryllium

The sorption isotherm was studied by recovering phosphorus and beryllium with the obtained sorbents from seawater with the addition of various concentrations of stable phosphorus and beryllium for 48 h. Each experiment was repeated several times (three series of three experiments for each concentration).

3. Results and Discussion

The physicochemical parameters of sorption of stable phosphorus and beryllium by the obtained sorbents and granular aluminum oxide were compared. Aluminum oxide was chosen because it was previously used for recovery of ^7Be from seawater [1] and ^{32}P , ^{33}P from rainwater [21].

3.1. Optimization of Conditions for Obtaining Sorbents PAN- $\text{Fe}(\text{OH})_3$

The methods for obtaining sorbents were described earlier in [18].

The effect of the initial concentration of NaOH in the initial impregnation solution upon receipt of Fe-EGSF and Fe-SF on the sorption parameters of phosphorus and beryllium is presented in Table 1.

It is shown that for Fe-EGSF, the best sorption rates are observed when using 40% NaOH. This is explained by the fact that during the production of Fe-EGSF, the production of electrochemically generated Na_2FeO_4 proceeds better in a more concentrated alkali solution; in addition, alkali is spent on the production of Na_2FeO_4 , and by the time the fiber is impregnated, its concentration in the solution drops.

Table 1. Influence of the initial concentration of NaOH in the initial impregnation solution in the preparation of Fe-EGSF and Fe-SF on the sorption parameters of phosphorus and beryllium.

C_{NaOH} , %	Parameter	Fe-EGSF		Fe-SF	
		P	Be	P	Be
10	K_d , mL/g	454	161	4100	1140
	R , %	81.9	61.7	97.6	91.9
	q , mg/g	0.0074	0.0160	0.0088	0.0238
20	K_d , mL/g	587	210	1450	402
	R , %	85.4	67.7	93.5	80.1
	q , mg/g	0.0077	0.0175	0.0085	0.0207
30	K_d , mL/g	915	359	726	251
	R , %	90.1	78.2	87.9	71.5
	q , mg/g	0.0082	0.0203	0.0080	0.0185
40	K_d , mL/g	1700	653	521	289
	R , %	94.4	86.7	83.9	74.3
	q , mg/g	0.0085	0.0225	0.0076	0.0192

When receiving Fe-SF, the best sorption rates are observed when using 10% NaOH. This is due to the fact that at higher alkali concentrations, the alkaline hydrolysis of the fiber is more intense. However, we have established earlier [18] that it is impossible to obtain a fiber using ready-made Na_2FeO_4 after alkaline hydrolysis. Experiments have shown that $\text{Fe}(\text{OH})_3$ is not fixed on hydrolyzed acrylic fiber, being almost completely washed off when the product is washed with water, resulting in a fiber that is slimy to the touch. Thus, at an alkali concentration in the solution of more than 10%, the process of alkaline hydrolysis proceeds more intensively, interfering with the fixation of $\text{Fe}(\text{OH})_3$ on the fiber.

The influence of the concentration of NaOH used for alkaline hydrolysis in the production of Fe-H on the parameters of sorption of phosphorus and beryllium are presented in Table 2.

Table 2. Influence of the NaOH concentration used for alkaline hydrolysis in the production of Fe-H on the sorption parameters of phosphorus and beryllium.

C_{NaOH} , %	P			Be		
	K_d , mL/g	R , %	q , mg/g	K_d , mL/g	R , %	q , mg/g
10	5730	98.3	0.0094	648	86.6	0.0224
20	61,500	99.8	0.0095	735	88.0	0.0228
30	7080	98.6	0.0094	521	83.9	0.0217
40	3610	97.3	0.0093	360	78.3	0.0203

It is shown that for Fe-H, the best sorption rates are observed when using 20% NaOH at the stage of alkaline hydrolysis during fiber production. This is most likely due to the fact that at higher alkali concentrations, the transition of the nitrile fiber to the carboxyl form is too intense, and at 10%, it is insufficient.

3.2. Sorption Kinetics of Stable Isotopes of Phosphorus and Beryllium

The results of studying the sorption kinetics of phosphorus and beryllium are shown in Figure 1.

The time to achieve sorption equilibrium in the recovery of phosphorus and beryllium for most sorbents is 32–48 h; for the Fe-H sorbent in the recovery of beryllium, it is 10 min. The data for the Fe-H sorbent during the recovery of beryllium are extremely different from all the studied sorbents; therefore, to verify them, the experiment was repeated several times.

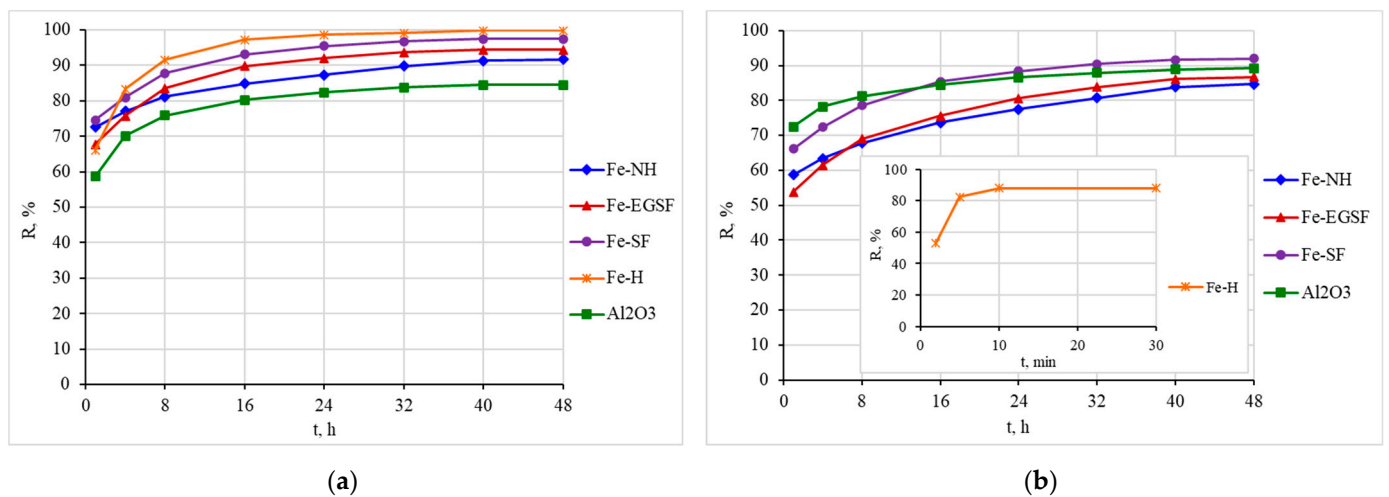


Figure 1. The dependence of the sorption efficiency on the time of sorption: (a) phosphorus; (b) beryllium.

The established dependences of the recovery of phosphorus and beryllium were described using the following models of sorption kinetics (Table 3):

- Intraparticle diffusion model [22]:

$$q_t = K_I \cdot t^{0.5} + c, \tag{1}$$

where K_I is the rate constant of intraparticle diffusion; c is the constant determining the contribution of the boundary layer, mg/g; q_t is the capacity of the sorbent at time t , mg/g; and t is the time, h.

- Pseudo-first-order model [22–25]:

$$\ln(q_e - q_t) = \ln q_e - K_1 \cdot t, \tag{2}$$

where q_e is the equilibrium capacity of the sorbent and mg/g; K_1 is the pseudo-first-order rate constant, h^{-1} .

- Pseudo-second-order model [22–24,26]:

$$\frac{t}{q_t} = \frac{1}{K_2 \cdot q_e^2} + \frac{1}{q_e} \cdot t, \tag{3}$$

where K_2 is the pseudo-second-order rate constant, g/mg·h.

- Elovich model (simplified by Chen and Clayton) [23,24,27]:

$$\ln q_e = \frac{1}{\beta} \cdot \ln(\alpha \cdot \beta) + \frac{1}{\beta} \cdot \ln t, \tag{4}$$

where α is the initial recovery rate constant, g/mg·h; and β is the desorption constant, g/mg.

Table 3. The obtained parameters of kinetic models.

Element	Sorbent	Intraparticle Diffusion			Pseudo First Order			Pseudo Second Order			Elovich Model			$q_{e, exp}$, mg/g
		K_I , mg/g·h ^{0.5}	c , mg/g	r^2	K_1 , h ⁻¹	q_e , mg/g	r^2	K_2 , g/mg·h	q_e , mg/g	r^2	α , g/mg·h	β , g/mg	r^2	
P	Fe-NH	0.0004	0.0088	0.975	0.096	0.0032	0.906	89.8	0.0115	0.999	1410	1670	0.981	0.0114
	Fe-EGSF	0.0006	0.0084	0.892	0.215	0.0095	0.775	88.2	0.0120	0.999	10.2	1110	0.982	0.0117
	Fe-SF	0.0006	0.0084	0.892	0.108	0.0030	0.998	106	0.0119	0.999	61.5	1250	0.982	0.0118
	Fe-H	0.0007	0.0088	0.797	0.122	0.0034	0.965	104	0.0129	1.00	3.28	909	0.940	0.0126
	Al ₂ O ₃	0.0005	0.0076	0.848	0.203	0.0073	0.788	107	0.0107	0.999	9.43	1250	0.980	0.0105
Be	Fe-NH	0.0011	0.0137	0.994	0.078	0.0082	0.927	23.2	0.0224	0.998	4.06	556	0.954	0.0212
	Fe-EGSF	0.0014	0.0127	0.968	0.092	0.0102	0.960	25.9	0.0216	0.998	0.627	435	0.983	0.0217
	Fe-SF	0.0011	0.0167	0.942	0.095	0.0048	0.957	35.3	0.0242	0.999	12.5	526	0.984	0.0238
	Fe-H	0.0403	0.0079	0.840	43.6	0.0453	0.996	3040	0.0241	0.999	16.7	313	0.698	0.0233
	Al ₂ O ₃	0.0007	0.0181	0.941	0.105	0.0084	0.971	62.9	0.0225	0.999	15,400	909	0.998	0.0223

Thus, to describe the sorption kinetics of phosphorus and beryllium by the studied sorbents, the pseudo-second-order model turned out to be the most acceptable, as evidenced by the highest correlation coefficients $r^2 = 0.999\text{--}1.00$ and consistent experimental and theoretical values of the equilibrium sorption capacity q_e .

Kinetic models of the pseudo-first-order, intraparticle diffusion, and Elovich models do not allow a good description of the sorption kinetics of phosphorus and beryllium.

Since the pseudo-second-order mechanism adequately describes the obtained values, the sorption process is limited by the ion exchange reaction, the sorbate and the functional group of the sorbent interact with each other in a ratio of 1:1 [23,26].

The highest calculated value of the rate constant K_2 (Table 3) of the pseudo-second-order was obtained for the recovery of phosphorus for the sorbents Fe-SF, Fe-H and $\text{Al}_2\text{O}_3 > 100$ g/mg·h, for which the time to reach the sorption equilibrium is 32 h; for the recovery of beryllium—for the Fe-H sorbent—this value was 3040 g/mg·h, for which the time to reach the equilibrium of sorption is 10 min.

The obtained values of the recovery rate constants for the intraparticle diffusion model, the Elovich model, and the pseudo-second-order model generally have the following regularities for sorbents based on $\text{Fe}(\text{OH})_3$:

- For phosphorus recovery:

$$\text{Fe-SF} > \text{Fe-H} > \text{Fe-NH} > \text{Fe-EGSF},$$

- For phosphorus recovery:

$$\text{Fe-H} > \text{Fe-SF} > \text{Fe-EGSF} > \text{Fe-NH}.$$

In addition, it should be noted that the rate at which sorption equilibrium is reached can be judged by the value of the Elovich desorption constant β ; at a fast rate, it is at its maximum [27].

3.3. Sorption Isotherm of the Stable Isotopes of Phosphorus and Beryllium

Figure 2 shows the results of studying the phosphorus sorption isotherm, and Figure 3 shows the results of studying beryllium.

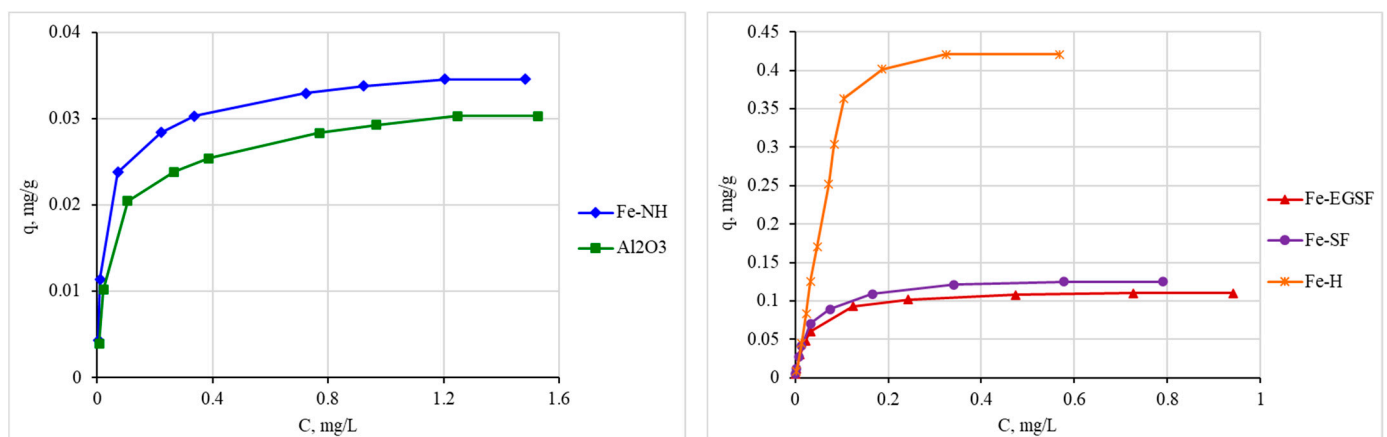


Figure 2. Phosphorus sorption isotherms.

The maximum capacity of sorbents for phosphorus is established at an equilibrium concentration of phosphorus in a solution of more than 0.4 mg/L, and for beryllium, it is established at an equilibrium concentration of beryllium in a solution of more than 2 mg/L. The Fe-H sorbent has the highest capacity for phosphorus and beryllium.

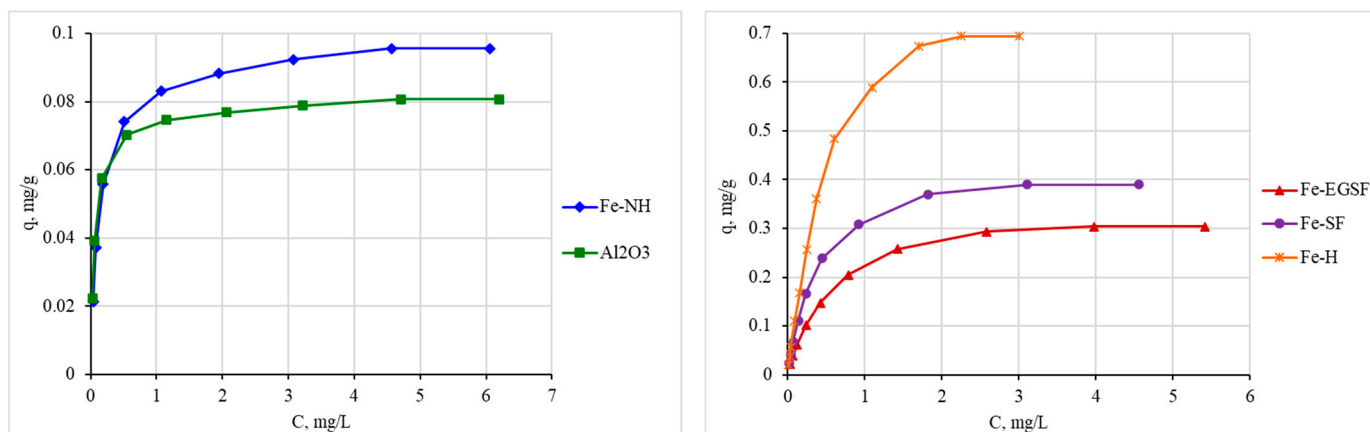


Figure 3. Beryllium sorption isotherms.

The established dependences of the recovery of phosphorus and beryllium were described using the following models of sorption isotherms:

- Langmuir model [22,25,27–29]:

$$\frac{1}{q_e} = \frac{1}{K_L \cdot q_m \cdot C_e} + \frac{1}{q_m}, \quad (5)$$

where q_m is the maximum capacity of the sorbent, mg/g; C_e is the equilibrium concentration, mg/L; and K_L is the Langmuir adsorption equilibrium constant, L/mg.

- Freundlich model [23,25,27–29]:

$$\lg q_e = \lg K_F + \frac{1}{n} \lg C_e, \quad (6)$$

where K_F is the Freundlich constant, mg/g; and n is an exchange center heterogeneity indicator.

- Dubinin–Radushkevich model [22,27,30]:

$$\ln q_e = \ln q_m - \beta \varepsilon^2, \quad (7)$$

where β is a constant characterizing energy of sorption, mol²/kJ²; ε is the Polanyi potential, kJ/mol, which shows the isothermal work required for the transfer of one mole of an ion to the surface of the sorbent from the volume of the equilibrium solution and calculated from the expression:

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right), \quad (8)$$

where R is the universal gas constant, 8.314×10^{-3} kJ/mol·K, T is the absolute temperature, K; and C_e is the equilibrium concentration, mol/m³.

The Dubinin–Radushkevich model makes it possible to evaluate the nature of the recovery of the sorbate on the sorbent and can be used to determine the average free energy of sorption [28,30]:

$$E = \frac{1}{(2\beta)^{0.5}}. \quad (9)$$

In a number of works [31–33], it is said that the value of the average free energy of sorption makes it possible to judge the nature of sorption. However, we [28] and other researchers [30] explained in detail that this isotherm does not make it possible to decipher the mechanism of sorption since it does not take into account the influence of the following factors: solvent on the chemical state of dissolved substances, surface charge and dissociation of functional groups of the sorbent in a solid/solution system [28,30].

Table 4 shows the determined parameters of the sorption isotherms. The obtained values show that the experimental data of phosphorus and beryllium recovery by all the studied sorbents are well described by the Langmuir sorption isotherm equation.

Table 4. The obtained parameters of the sorption isotherms.

Element	Sorbent	Langmuir Isotherm			Freundlich Isotherm			Dubinin–Radushkevich Isotherm			
		g_m , mg/g	K_L , L/mg	r^2	K_F , mg/g	n	r^2	g_m , mg/g	β , mol ² /kJ ²	E , kJ/mol	r^2
P	Fe-NH	0.035	39.3	0.995	0.040	3.10	0.888	0.050	0.0043	10.8	0.946
	Fe-EGSF	0.111	38.8	0.999	0.195	2.14	0.896	0.218	0.0055	9.53	0.957
	Fe-SF	0.126	34.7	0.999	0.260	1.95	0.908	0.273	0.0059	9.21	0.961
	Fe-H	0.425	6.02	0.997	1.40	1.28	0.884	1.96	0.0100	7.07	0.951
	Al ₂ O ₃	0.030	20.6	0.999	0.034	2.76	0.904	0.046	0.0052	9.81	0.958
Be	Fe-NH	0.096	7.48	0.999	0.073	3.47	0.886	0.105	0.0080	7.91	0.979
	Fe-EGSF	0.304	2.28	0.999	0.192	1.78	0.956	0.349	0.0146	5.85	0.998
	Fe-SF	0.392	3.04	0.999	0.290	1.75	0.948	0.471	0.0133	6.13	0.997
	Fe-H	0.712	2.24	0.999	0.506	1.50	0.962	0.871	0.0148	5.81	0.995
	Al ₂ O ₃	0.081	14.3	0.998	0.067	4.56	0.842	0.088	0.0059	9.21	0.955

The constant n indicates the intensity of the sorbent-sorbate interaction. Thus, sorption proceeds well even at high concentrations of phosphorus and beryllium ions, as evidenced by n values greater than 1 [25,27].

These materials can be successfully used to study various oceanological processes, such as vertical transport [34], and phosphorus biodynamics [35] by radiotracer methods.

4. Conclusions

The physicochemical characteristics of phosphorus and beryllium recovery from seawater by sorbents based on PAN and Fe(OH)₃ obtained using various impregnation methods have been studied.

The obtained dependences of the sorption efficiency of phosphorus and beryllium on the sorption time were described using models of intraparticle diffusion and the pseudo-first-order, pseudo-second-order, and Elovich model. It was established that the sorption process is limited by the ion exchange reaction.

The time to reach sorption equilibrium for each sorbent was established. The time to achieve sorption equilibrium in the recovery of phosphorus and beryllium for most sorbents is 32–48 h, while the time for the Fe-H sorbent in the recovery of beryllium is 10 min.

The dependence of the sorbent capacities on the equilibrium concentrations of phosphorus and beryllium in solution was established. The maximum capacity of sorbents for phosphorus was established at an equilibrium concentration of phosphorus in a solution of more than 0.4 mg/L, and for beryllium, it was established at an equilibrium concentration of beryllium in a solution of more than 2 mg/L. The Fe-H sorbent has the highest capacity for phosphorus and beryllium. The obtained values were characterized using the Langmuir, Freundlich, and Dubinin–Radushkevich sorption isotherm models. The sorbents Fe-H and Fe-SF showed the highest capacitance characteristics for phosphorus and beryllium.

Optimal conditions for obtaining sorbents based on PAN and Fe(OH)₃ have been established. The effect of the initial concentration of NaOH in the initial impregnation solution in the preparation of Fe-EGSF and Fe-SF sorbents and in the solution used for alkaline hydrolysis in the preparation of the Fe-H sorbent is shown.

Author Contributions: N.A.B.—obtaining the sorbents, sorption experiments, discussion of the results, preparation of an article; M.A.F.—obtaining sorbents, sorption experiments; O.N.K.—measurement of stable phosphorus; E.V.S., I.G.S.—measurement of stable beryllium, participation in expeditionary work; I.G.T.—discussion of the results, preparation of the article. All authors have read and agreed to the published version of the manuscript.

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