Research article

Peculiarities of adsorption of Cr (VI) ions on the surface of *Chlorella vulgaris ZBS1* algae cells

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ABSTRACT

Cr (VI) compounds are the most dangerous for human health and the environment, therefore, the study of their adsorption features is of great interest. A comprehensive study of the adsorption of Cr (VI) ions on the surface of *Chlorella vulgaris ZBS1* algae cells was carried out evaluating the effect of the pH of the medium on the degree of removal of Cr (VI) ions from solutions and on the zeta potential of the cell surface was. The highest values of the degree of removal of Cr (VI) ions equal to 94.6–95.4% are achieved in the pH range of 1–2, being the result of the electrostatic attraction of $HCrO_4^-$ groups to protonated amino groups of the cell surface and the possibility of reducing Cr (VI) ions to Cr (III) in an acidic medium, followed by the formation of Cr (III) ions of coordination bonds with amine and carboxyl groups of algae cells.

The adsorption data were processed within the framework of Langmuir, Freundlich, Dubinin-Radushkevich and Temkin models. It was shown that the maximum Langmuir adsorption value was 74.63 mg/g. The values of the adsorption parameters $1/n$ and K_f in the Freundlich model were equal to 0.713 and 2.82 mg/g. In the Dubinin-Radushkevich model, the maximum adsorption capacity (q_m) and free energy (E) were equal to 39.73 mg/g and 2.604 kJ/mol, respectively. Whereas, according to the Temkin model, the constant A was equal to 18.215 L/mg, and b_T was equal to 0.023 kJ/mol. Taking into account the low values of free energy, it is concluded that adsorption is caused by non-covalent interactions.

The study of adsorption kinetics showed that the adsorption of Cr (VI) ions on the surface of *Chlorella vulgaris ZBS1* algae cells is described in the framework of the pseudo-second order model. The kinetic behavior of the process is discussed in the framework of the IPDM and ELM models. With increasing temperature, the constant of intraparticle diffusion of Cr (VI) ions decreases, which is explained with increasing of hydrophobic interactions between nonpolar sites of protein macromolecules and polysaccharides in the composition of algae cells. The increase in the adsorption of Cr (VI) ions at pH 8.62 in the temperature range of 298–353 K is justified by the shrinkage of the biosorbent volume, which leads to the blocking of a part of the anionic groups on the surface of algae cells. Therefore, the decrease in the electrostatic repulsion between the negatively charged surface of the adsorbent and Cr (VI) oxyanions is observed.

1. Introduction

Recently, water purification from heavy metal ions is one of the urgent tasks [1, 2]. Among environmental pollutants, heavy metal ions are the most dangerous because they are toxic and cannot be decomposed [3]. Chromium compounds in the environment exist in two forms: Cr (III) and Cr (VI), Cr (VI) is much more toxic than Cr (III), and is more soluble in aqueous and soil media [4, 5]. The greatest pollution of waste water with Cr (VI) ions comes from the paint and leather industries, textile, mining, and steel making [6, 7, 8, 9], whereas Cr (III) ions are contained mainly in wastes released from the waste waters of hospitals and a tannery [10, 11].

Chromium (VI) compounds are highly carcinogenic, so their presence in water and soil can cause various diseases, such as lung cancer, respiratory tract diseases, diarrhea, kidney, liver and stomach damage [12, 13]. But the most dangerous thing is that this metal can pass through cell

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membranes, attack DNA, proteins, and membrane lipids, which, of course, will lead to a violation of the integrity of cells of living organisms [14, 15]. According to World Health Organization standards, the concentration of chromium (VI) ions in drinking water, surface water and industrial waste water should not exceed 0.05 mg/L, 0.1 mg/L and 0.25 mg/L, respectively [16]. However, currently their content in wastewater is 5–220 mg/L, which significantly exceeds the permissible norm. Therefore, the removal of Cr (VI) ions from water is more important than the control of water pollution by Cr (III) ions [17].

There are various methods for removing and concentrating heavy metals from water and waste water: precipitation, coagulation, reverse osmosis, ion exchange, electrolysis and adsorption [18]. The adsorption method is the simplest and the most convenient for use in water purification. However, the efficiency of adsorption depends on the properties of the adsorbent and the conditions of the process. The most effective for removing toxic metal ions from water are natural adsorbents: coal, clay, zeolites, peat moss and chitin [19, 20]. Along with them, the use of agricultural waste for water purification, such as walnut shells, rice husks, and plant leaves, is becoming widespread [21, 22, 23].

Composite and modified nanosorbents show high efficiency in optimizing water purification conditions from heavy metal ions [24, 25, 26, 27, 28, 29, 30]. The use of biomass of brown algae *Sargassum oligocystum*, pre-modified $CaCl_2$, for the treatment of water, containing Cr (VI) ions provides an adsorption value of 34.46 mg/g [3]. Optimization of adsorption conditions according to various parameters (pH, temperature, biosorbent dose, contact time) leads to the achievement of the degree of removal of Cr (VI) ions from water 96%. Bentonite/bio-coal composite based on clay and apricot leaves was used for rapid extraction of Cr (VI) ions from synthetic wastewater [5]. The transition from a clay sorbent to a composite sorbent increases the adsorption of Cr (VI) ions from 59.527 mg/g to 64.102 mg/g. At the same time, the degree of removal of Cr (VI) ions increases from 47.16% to 98.47%.

The possibility of removal of Pb (II) and Cd (II) ions from aqueous solutions, shipyard wastewater and landfill leachate by modified *Rhizopus oryzae* biomass was shown by Naeimi et al. [31]. Under optimal conditions, the maximum degree of removal of Pb (II) and Cd (II) ions was 95.66% and 94.55%, respectively. To facilitate the process of separating sorbents from water, it is proposed to use the magnetic nanocomposite eggshell/starch/Fe_3O_4 [28]. At a concentration of Cd (II) and Pb (II) ions in a solution of 10 mg/L, pH range 6–7, a temperature of 25 °C, an adsorbate/adsorbent contact time of 60 min and a stirring speed of 500 rpm, the degree of removal of Cd (II) and Pb (II) ions was equal to 96.38% and 97.56%, respectively. The adsorption efficiency is justified by the presence of a large number of active centers on the magnetic nanocomposite.

The use of nanoparticles of the magnetic composite *Moringa olifera* tree activated carbon-chitosan-Fe_3O_4 makes it possible to eliminate up to 99.75% of Cr (VI) ions from the solution [32]. This inexpensive composite adsorbent withstands 9-fold use with a slight decrease in the degree of removal of Cr (VI) ions. Magnetic composites polydopamine/modified hydroxyapatite/Fe_3O_4 were used to removal Zn (II) ions from aqueous solutions [33]. At the same time, along with parameters such as the pH of the medium, the initial concentration of metal ions and the dose of the adsorbent, ultrasonic power and ultrasonic time were changed. Their increase contributed to an increase in the adsorption of Zn (II) ions to 46.37 mg/g, which corresponds to almost 100% extraction of Zn (II) ions from solutions.

Various groups of biomaterials based on bacteria, fungi, yeast and algae have been studied as biosorbents for bioremediation of heavy metals [34, 35]. The fungus *B. bassiana* showed an average of 84.5% extraction from a mixture of several metal ions, i.e. Zn (II), Cu (II), Cd (II), Cr (VI), and Ni (II) in the pH range the 6–8 [36]. The authors [37] found that the immobilized cells of *Sargassum sp.* Are the excellent biosorbent for the extraction of Ni (II) and Cu (II) from aqueous solutions.

The potential possibility of using three algae *Cladophora glomerata*, *Enteromorpha intestinalis* and *Microspora amoena* to extract Cr (VI) ions

from aqueous solutions has been studied [38]. Among them, the cells of the microalgae *Cladophora glomerata* showed the maximum removal of Cr (VI) ions equal to 66.6% in the pH of 2.0. These cells have been selected as a suitable sorbent for removing Cr (VI) ions from aqueous solutions. It was shown Al-Homaidan et al. [39] that at low concentrations of heavy metals, the cells of *Chlorella coloniales* algae showed their effectiveness for bioaccumulation of Cr, Co, Fe and As with a degree of removal of 90.3–99.0%, at high concentrations of heavy metals, the degree of removal were 95.1–97.8%, respectively.

The pH of the medium is one of the most important variables in the removal of toxic metals from solutions, as it affects both the state of metal ions and the ionization of sorbents [40]. On the other hand, the Cr (VI) ions that are subject to significant changes in solution depending the environmental conditions [41], therefore, the analysis of their adsorption features is of theoretical interest. It is also known that the functional groups of microbial cells can affect the state of Cr (VI) ions in solution [42]. However, the widespread use of microbial cells to extract metal ions from solutions is limited by the lack of quantitative data on their sorption capacity and the mutual influence of metal ions and biosorbents on each other, as well as the influence of the surface properties of microbial cells on their sorption properties. At the same time, biosorbents based on microbial cells have advantages over other sorbents such as biocompatibility, low cost, ability to decompose, non-toxicity and the possibility of reuse [3].

In this regard, the purpose of this study was to determine the features of adsorption of Cr (VI) ions on the surface of *Chlorella vulgaris ZBS1* algae cells taking into account the surface properties of algae cells, the medium pH and the mutual influence of Cr (VI) ions and cells on each other.

2. Experimental part

2.1. Preparation of materials

Chlorella vulgaris ZBS1 (strain) algae cells were cultured in an illuminated, thermostated medium at 298 K, medium composition (g/L): $NaNO_3$—1.50; K_2HPO_4—0.03; EDTA—0.001; $MgSO_4 \bullet 7H_2O$—0.075; $CaCl_2$—0.02; citric acid—0.006; ammonium iron citrate—0.006. The cells were separated from the culture medium by centrifugation (7000 rpm, 5 min), then washed three times with distilled water to remove the remaining medium.

Potassium dichromate salts $K_2Cr_2O_7$ (Sigma Aldrich, USA) were used to prepare solutions containing Cr (VI) ions. The stock Cr (VI) solution (104 mg/L) was prepared by dissolving 0.0735 g of potassium dichromate ($K_2Cr_2O_7$) in 250 mL of deionized water. In the future, this solution was diluted to the required concentration. Solutions with an initial concentration $K_2Cr_2O_7$ 10.4–104.0 mg/L were used in adsorption experiments.

2.2. Experimental methods

2.2.1. Adsorption of Cr (VI) ions on the surface of Chlorella vulgaris ZBS1 algae cells

Initial solutions for adsorption of Cr (VI) ions on the surface of *Chlorella vulgaris ZBS1* algae cells were obtained by dissolving potassium dichromate salt $K_2Cr_2O_7$ in bidistilled water. Working solutions were obtained by diluting the stock solutions with bidistilled water. To adsorb Cr (VI) ions on the surface of *Chlorella vulgaris ZBS1* algae cells, 10 mL of algae suspension was mixed with 10 mL of Cr (VI) salt solution of different concentrations and the mixture was kept for 2 h at a temperature of 298 K. The mixture was then centrifuged for 3 min at 5000 rpm to separate the adsorbent from the solution. The separated solution was analyzed using for the content of chromium ions an Agilent 240FS atomic adsorption spectrophotometer (USA). The accuracy of the analysis was <3%.

The adsorption of chromium (VI) ions on the surface of *Chlorella vulgaris ZBS1* algae cells was calculated by using the following formula (1):

$$q_e = \frac{(C_0 - C_e) \cdot V}{m} \quad (1)$$

where: q_e is the adsorption value (mg/g); C_0 is the initial concentration of Cr (VI) ions, (mg/L); C_e is the equilibrium concentration of Cr (VI), (mg/L); V is the volume of the solution (L); m is the mass of algae (g).

The degree of removal (R) Cr (VI) ions in is calculated by formula (2):

$$R = \frac{(C_0 - C_e)}{C_0} \cdot 100\% \quad (2)$$

where: C_0 and C_e are the initial and equilibrium concentration of Cr (VI) ions in solution (mg/L).

The effect of pH on the adsorption of Cr (VI) ions was studied by varying its value from 1.0 to 9.0 using solutions of 0.05 mol/L NaOH and 0.05 mol/L HCl. pH measurements were carried out at a temperature of 298 ± 2 K. The experimental error did not exceed 4%.

2.2.2. FTIR spectroscopy and scanning electron microscopy (SEM)

FTIR spectroscopic analysis was performed on a PerkinElmer Spectrum 65 FTIR device (USA) in KBr tablets. 20 ml of *Chlorella vulgaris ZBS1* algae suspension was mixed with 20 mL of Cr (VI) salt solution at 10^{-2} mol/L concentrations, and then the adsorbent was separated from the solution. The initial and separated algae cells from the $K_2Cr_2O_7$ solution were dried for 24 h at the temperature of 353 K, then pressed with KBr in a ratio of 2:250 (mg/mg). The studies were carried out in the frequency range of 450–4000 cm^{-1} with a spectral resolution of 4 cm^{-1} with 20 scans for each sample.

For SEM analysis tests, dried samples of algae cells were used, initial and separated from the $K_2Cr_2O_7$ solution at the temperature of 353 K, since very low and high temperatures negatively affect the cell structure. Drying at the medium temperatures (353 K) preserves the cellular structure [43]. The images were taken at an accelerating voltage of 10–20 kV using a scanning electron microscope Quanta 200i 3D (FEI Company, USA).

2.2.3. Determination of the zeta potential of cells

The zeta potential of algae cells was determined by measuring electrophoretic mobility in combination with light scattering on the Malvern ZetaSizer NanoZS device (Malvern, UK). At least 30 readings of electrophoretic mobility were measured for each sample, from which the average values were calculated.

2.2.4. Kinetic and thermodynamic study of adsorption

Kinetic studies of the adsorption of Cr (VI) ions on the surface of *Chlorella vulgaris ZBS1* algae cells were carried out at a constant pH value of 8.62. After mixing the $K_2Cr_2O_7$ solution with a suspension of *Chlorella vulgaris ZBS1* cells, samples of the solution were taken for analysis for the content of Cr (VI) ions every 20 min, for 120 min. The effect of temperature on the adsorption equilibrium was investigated by varying the temperature from 298 to 328 K. To study the kinetic behavior of the adsorption process of Cr(VI) from aqueous solutions, kinetic models of pseudo-first order, pseudo-second order, the Morris-Weber model describing intraporous diffusion, and the Elovich model were used; calculations were carried out according to formulas (3, 4, 5, and 6) [3, 26, 27, 28, 29, 30, 31, 32, 44]:

$$\ln(q_e - q_t) = \ln q_e - t k_1 \quad (3)$$

$$\frac{t}{q_t} = \left(\frac{1}{k_2 q_e^2}\right) + \frac{t}{q_e} \quad (4)$$

$$q_t = K_{int}\sqrt{t} + C_i \quad (5)$$

$$q_t = \frac{1}{\beta}\ln(1 + \alpha\beta t) \quad (6)$$

here, q_t and q_e are the adsorption capacity of Cr (VI) per gram of adsorbent (mg/g), k_1 (1/min)—the constant adsorption rate, k_2 (g/mg·min)—the constant quasi-square velocity of the kinetic model. K_{int}—the constant diffusion rate inside the particles, C_i—corresponds to the effects of the boundary layer, α—the initial adsorption rate (mg/g·min), β—the desorption constant (g/mg).

3. Results and discussion

3.1. Structure of the adsorbent surface

The cells of *Chlorella vulgaris* algae have the shape of a sphere with an average diameter of 2–8 microns [45]. The study of *Chlorella vulgaris ZBS1* algae cells using scanning electron microscopy showed that they are spherical particles with a size of about 2–3 microns, having a rough surface with clearly defined micropores (Figure 1a). Comparison of cell morphology before and after adsorption of Cr (VI) ions shows that it has changed from an irregular and porous structure promoting the adsorption of Cr (VI) ions to a smoother surface (Figure 1b). In addition, after the adsorption of chromium ions on it, such changes as shrinkage and adhesion of layers caused by the action of Cr (VI) ions on them are noticeable. It should also be noted here that algae as marine organisms can secrete extracellular polymeric substances that help them form a protective and hydrated microenvironment for the survival under the stress [46]. In all likelihood, the cells of algae *Chlorella vulgaris ZBS1* are also covered with such polymeric substances.

3.2. Adsorption of Cr (VI) ions on the surface of Chlorella vulgaris ZBS1 algae cells

Green algae, when used as adsorbents, have some additional advantages over other microorganisms due to their large surface area, large volume of mucus with high binding affinity and simple nutrient requirements [47].

To study the adsorption of Cr (VI) ions on the surface of *Chlorella vulgaris ZBS1* algae cells and obtain data on adsorption equilibrium, various models of adsorption isotherms were used: Langmuir, Freundlich, Dubinin-Radushkevich, and Temkin one [24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 48, 49].

The Langmuir model assumes that the adsorption of metal ions occurs on single-layer and homogeneous surfaces without any interaction between adjacent sites on the adsorbent. This model contains also information about the adsorption capacity and the equilibrium behavior of the adsorption process. To get this information the Langmuir equation must be linearized (7):

$$\frac{C_e}{q_e} = \frac{1}{K_L Q_m} + \frac{C_e}{Q_m} \quad (7)$$

where: Q_m and K_L represent the adsorption capacity (mg/g) and adsorption energy (L/g), respectively, they are considered as constants of the Langmuir model.

The Freundlich model is also utilized to explain the adsorption process on inhomogeneous and multilayer surfaces. The linear form of the Freundlich model is following (8):

$$\ln q_e = \ln K_f + \frac{1}{n}\ln C_e \quad (8)$$

where: K_f and n are the constants of the Freundlich model, representing the relationship between adsorption capacity and adsorption intensity, respectively. To determine the parameters $1/n$ and K_f, $\ln q_e$ is constructed with respect to $\ln C_e$. It was reported that the value of n is 1–10. This parameter represents the physico-chemical type of the adsorption process. If n = 1, then the adsorption process is linear, if n > 1,
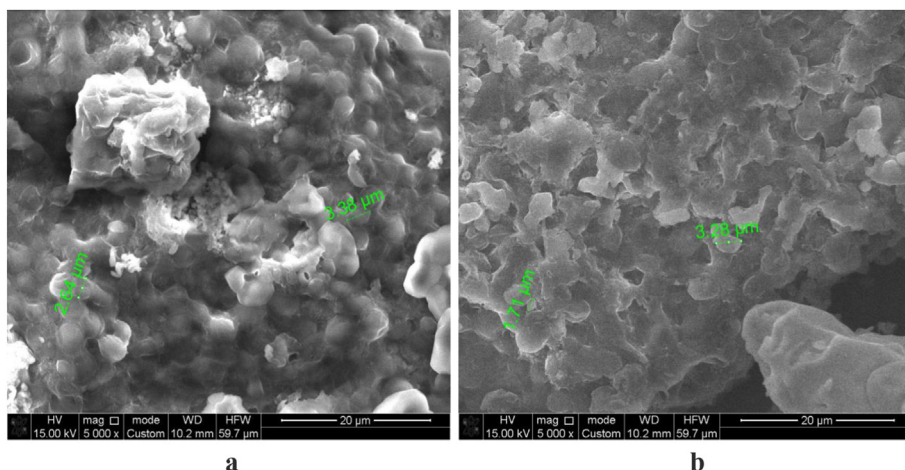
Figure 1. SEM images of *Chlorella vulgaris ZBS1* cells surface (a) before and (b) after adsorption of Cr (VI) ions.

adsorption is a favorable physical process, and if n < 1, it can be deduced that adsorption occurred as a result of chemical interactions [49].

The Dubinin-Radushkevich (D-R) model is based on the Polanyi potential theory [50] and is more general in comparison with the Langmuir model. It does not imply uniformity of the surface and constancy of the adsorption potential, which is why it is attractive for describing adsorption on the surface of algae cells. The Dubinin-Radushkevich model is also used to establish the physical or chemical nature of adsorption. Dubinin suggested that adsorption occurs in the volume of micropores of the adsorbent, in contrast to layered adsorption on the walls of micropores [51]. The linear form of the Dubinin-Radushkevich equation is following (9, 10):

$$q_e = q_m \exp\left(-\beta \varepsilon^2\right) \qquad (9)$$

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \qquad (10)$$

where: β (mol^2/J^2) and q_m (mg/g) represent the constants of the Dubinin-Radushkevich model, ε is the Polanyi potential, R is the universal gas constant, and T is the absolute temperature (K). The β and q_m constants of the Dubinin-Radushkevich isotherm model are obtained from the slope and intercept of the graph of the dependence of $\ln q_e$ on ε^2. The value of β parameter is used for calculating the mean free energy of adsorption (E, kJ/mol) based on the following Eq. (11):

$$E = \frac{1}{\sqrt{2\beta}} \qquad (11)$$

By the value of the free energy of adsorption, the type of adsorption process can be determined. If it is less than 8 kJ/mol, then the adsorption is physical, and if it is in the range of 8–16 kJ/mol, then the adsorption belongs to the ion exchange type [52]. Accordingly, higher values of free energy can be attributed to chemical adsorption.

The Temkin isotherm model includes a factor that fully takes into account the interaction between adsorbents and adsorbates. The Temkin isotherm suggests that the decrease in heat adsorption is rather linear and the linearized form of the Temkin adsorption isotherm is following (12, 13):

$$q_e = B \ln(A \times C_e) \qquad (12)$$

$$B = \frac{RT}{b_T} \qquad (13)$$

where: A (L/mg) and b_T (kJ/mol) are Temkin constants.

The Temkin adsorption model assumes that the adsorption centers in the adsorbent are not the same and have different coefficients and adsorption energies [44, 53]. If the adsorption sites are arranged in accordance with the decrease in the adsorption energy, then the change in the adsorption energy of Temkin will be proportional to the difference in the adsorption energy between two adjacent active centers.

The adsorption isotherms of Cr (VI) ions on the surface of *Chlorella vulgaris ZBS1* algae cells and the adsorption parameters found in the Langmuir, Freundlich, Dubinin-Radushkevich and Temkin models are shown in Figures 2 and 3(a, b, c, and d) respectively.

It turned out that the value of the correlation coefficient (R^2) is the maximum for the Freundlich isotherm (Figure 3(a, b, c, and d)). This suggests that the adsorption of Cr (VI) ions occurs on heterogeneous surfaces. The peculiarity of the Freundlich isotherm in this case is that it is an ascending curve. Indeed, microbial cells are not characterized by the saturation of the surface with metal ions, since they, in response to the presence of metal ions, bring new functional groups capable of capturing them to their surface. In addition, the cells of microorganisms are prone to bioaccumulate of metal ions as a nutrient [54]. The values of the parameters $1/n$ and K_f in the Freundlich model were determined as 0.713 and 2.82 mg/g, respectively (Table 1). The Freundlich constant $1/n$ is related to the adsorption energy measures and indicates the adsorption
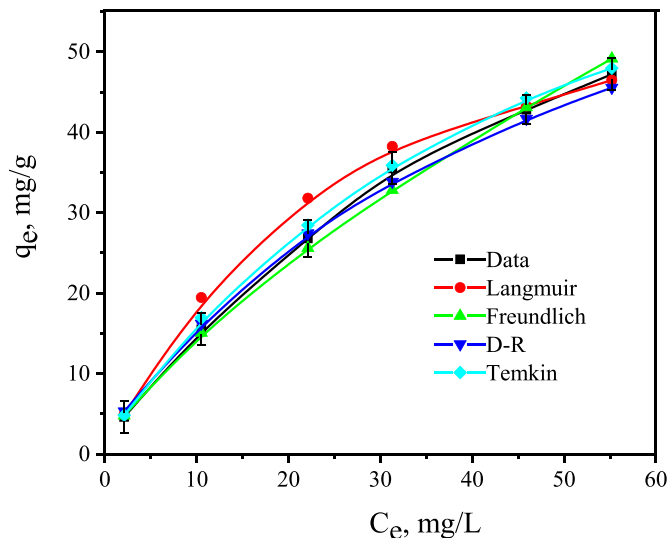

Figure 2. Adsorption isotherms of Cr (VI) ions on the surface of algae cells *Chlorella vulgaris ZBS1* (Temperature: 298 K, adsorbent dose = 0.125 g, C_0 = 10^{-3} mol/L, pH: 8.62, contact time: 120 min).
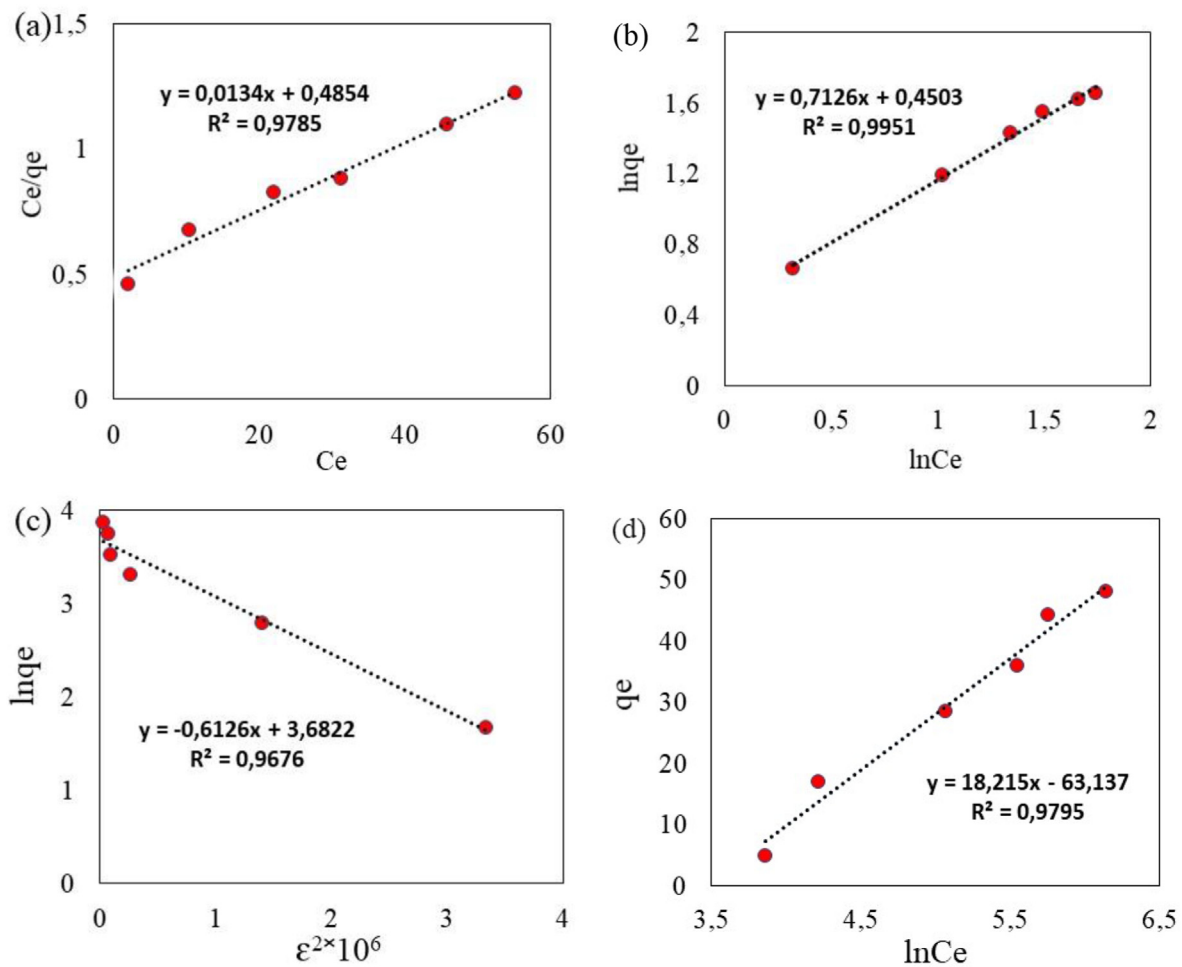
Figure 3. Adsorption isotherm plots of (a) Langmuir, (b) Freundlich, (c) Dubinin-Radushkevich, and (d) Temkin models for adsorption of Cr (VI) ions on the surface of *Chlorella vulgaris ZBS1* algae.

nature. The parameter $1/n$ in the range 0.5–1.0 is considered as favorable for adsorption [55]. The value of n equal to 1.40 indicates the physical nature of adsorption.

The maximum adsorption value (Q_m) according to the Langmuir model is 74.63 mg/g, and the Langmuir constant is 0.034 L/mg (Table 1). For the comparison, we note that the adsorption of Cr (VI) ions on the surface of *Halimeda gracilis* [56] and *Turbinaria ornata* [63] algae cells at pH 4.9–5.0 is 55.55 and 44.9 mg/g, respectively, but adsorption experiments were carried out at higher temperatures (Table 2).

According to calculations carried out within the Dubinin-Radushkevich model, the maximum adsorption (q_m) is 39.73 mg/g, and the free energy of the adsorption process (E) is 2.604 kJ/mol (Table 1). Given such a low value of free energy, it can be concluded that the adsorption of Cr (VI) ions on the surface of *Chlorella vulgaris ZBS1* algae cells is a physical process.

According to the Temkin model, the constant A is 18.215 L/mg, and the value b_T is 0.023 kJ/mol (Table 1). This energy value also shows that the interaction between the adsorbent surface and Cr (VI) ions is weak and, as a consequence, that the adsorption process may be physical type.

Based on the data on the adsorption of Cr (VI) ions on the surface of *Chlorella vulgaris ZBS1* algae cells and their processing within the framework of various models, it can be concluded that adsorption is predominantly physical, that is, due to non-covalent interactions. The adsorption value has values comparable to the adsorption of Cr (VI) ions on other types of algae.

3.3. Effect of the initial Cr (VI) concentration on adsorption

The efficiency of extraction of heavy metal ions especially depends on their initial concentration. With an increase in the initial concentration of Cr (VI) ions from 2.1 to 55.2 mg/l, the degree of their removal using *Chlorella vulgaris ZBS1* cells decreased from 75.46 to 46.08% (Figure 4).

At low concentrations of Cr (VI) salt, a high degree of removal is observed, which is due to the large surface area of the adsorbent

Table 1. The adsorption parameters of different isotherm models.

Models	Parameters	Adsorbent
		Chlorella vulgaris ZBS1 algae cells
Langmuir	K_L, L/mg	0.034
	Q_m, mg/g	74.63 ± 2.02
	R^2	0.9785
Freundlich	$1/n$	0.713
	K_f, mg/g	2.82
	R^2	0.9951
Dubinin-Radushkevich (D-R)	E, kJ/mol	2.604
	q_m, mg/g	39.73
	$\beta \times 10^6$, mol²/J²	0.001
	R^2	0.9676
Temkin	b_T, kJ/mol	0.023
	A, L/mg	18.215
	R^2	0.9795

Table 2. Comparison of maximum Cr (VI) adsorption on the surface of *Chlorella vulgaris ZBS1* algae cells with the literature data.

Adsorbent	Q_m, mg/g	pH	algal dose, g/L	T, K	Initial conc. Cr(VI), mg/L	t, min	References
Halimeda gracilis	55.55	4.9	2.2	308.15	50	60	[56]
Ulva compressa L.	21.66	2	6	323	25	96	[57]
S. bevanom	39.68	3	0.7	313	100	110	[58]
U. fasciata	47.62	1	0.05–0.25	298	25–100	60	[59]
Rhizoclonium hookeri	67.3	2	1	298	1000	40	[60]
Azolla Filiculoidus	10,638	2	0,1	298	20–100	100	[61]
Sargassum tenerrimum	37.7	2	2	298	10	240	[62]
Turbinaria ornate	44.95	5	0.27	306.6	100	215	[63]
Fusarium subglutinans	16.52	4	6	303	25–150	60	[64]
Chlorella vulgaris ZBS1	74.63	2	0.125	298	10–60	120	This study

available for adsorption. With an increase in the initial salt concentration, the degree of extraction of Cr (VI) ions gradually decreases due to a decrease in the number of free adsorption sites. This is evidence that the initial concentration of metal ions plays an important role in the efficiency of the adsorption process. The initial concentration provides an important driving force for overcoming the resistance to mass transfer of the metal ion between the aqueous and solid phases [65]. Moreover, it was found that a low concentration of heavy metals is a stimulator of microalgae growth due to the phenomenon of hormesis [66]. Its essence lies in the fact that the lowest concentrations of chemical, physical or biological factors can affect a bacterium, plant, animal, or person in the opposite direction.

The advantage of using algae cells for adsorption of Cr (VI) ions can be explained primarily by the fact that there are a large number of different functional groups on their surface that can bind to Cr (VI) ions. The diversity of these groups leads to the fact that they can bind to metal ions by various mechanisms. In addition, functional groups can influence the state of Cr (VI) ions [35].

3.4. The effect of Cr (VI) ions on the zeta potential of the cell surface

Most microbial cells have a negative charge, since the number of anionic functional groups on the surface of the cell wall exceeds the number of cationic ones. This leads to a greater adsorption capacity of cells in relation to metal ions [67].

Measurement of the zeta potential of *Chlorella vulgaris ZBS1* algae cells showed that their surface is negatively charged, the electrokinetic

potential is −12.5 mV at pH 8.62 (Figure 5). According to [68], the zeta potential of algae cells ranges from–(10–35) mV. The introduction of a $K_2Cr_2O_7$ salt solution into the suspension of algae cells leads to an increase in the negative value of the electrokinetic potential of cells up to −22.1 mV at a salt concentration of 10^{-4} mol/L, with a further increase in the salt concentration, the electrokinetic potential of the *Chlorella vulgaris* cell surface begins to decrease monotonically. According to [69], in the pH > 8 region, chromium ions are in the form of CrO_4^{2-} anions, so an increase in the negative charge of the surface of algae cells is quite expected. However, what is surprising is the decrease in the negative charge of the cell surface with an increase in salt concentration. Obviously, the accumulation of chromate ions in the solution in the form of K^+ ions leads to the neutralization of the charge of anionic groups and a corresponding decrease in the negative charge of the surface of algae cells.

3.5. The effect of the pH of the medium on the efficiency of removing Cr (VI) ions

The pH value is an important factor determining the form of metal ions in solution and the degree of ionization of functional groups of microbial cells [44]. pH significantly affects the state of the Cr (VI) solution, as well as the distribution of functional groups on the surface of microbial cells. In this regard, it is of interest to study the effect of the pH of the medium on the removal degree of Cr (VI) ions by algae cells.
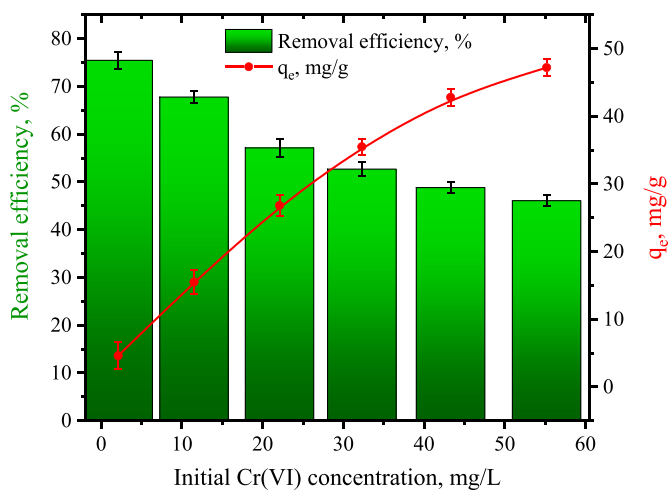
Figure 4. Effects of concentration Cr (VI) ions on adsorption and removal efficiency (Temperature: 298 K, adsorbent dose = 0.125 g, $C_0 = 10^{-3}$ mol/L, pH: 8.62, contact time: 120 min).
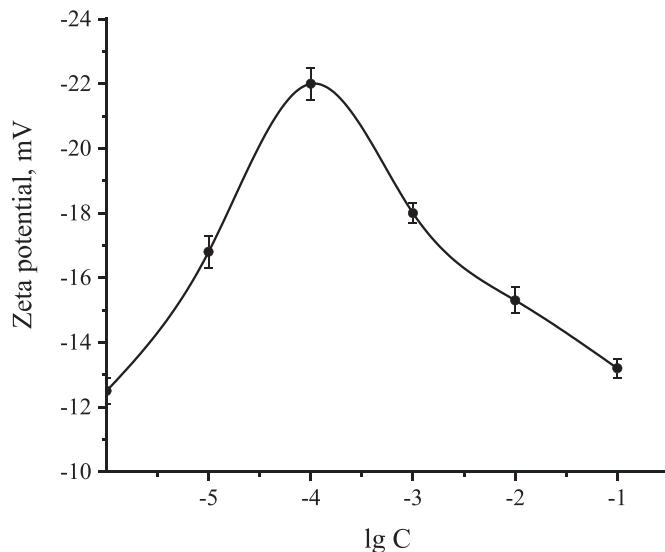
Figure 5. Effects of the concentration of Cr (VI) ions on the zeta-potential (adsorbent dose: 0.125 g/L, pH: 8.62, T: 298 K).

In the study, the pH value varied from 1 to 9. The effect of pH on the degree of removal of Cr (VI) ions using *Chlorella vulgaris ZBS1* algae cells is shown in Figure 6. It shows that the efficiency of removal of Cr (VI) ions is high (94.6–95.4%) at low pH values (pH 1–2), and with an increase in the initial pH values, the removal degree is significantly reduced.

As can be seen from Figure 7, showing the effect of the pH on the zeta potential of *Chlorella vulgaris ZBS1* algae cells, the isoelectric point pH_{zpc} is at a pH value of 2.0. The main functional groups of *Chlorella vulgaris ZBS1* algae cells are carboxyl, phosphate, sulfate and amine [70]. The high degree of removal of Cr (VI) ions at pH values 1–2 can be justified by the fact that under these conditions the amino groups of algae cells are protonated and acquire a positive charge, and Cr (VI) ions are in the form of $HCrO_4^-$. It should be noted here that at low pH values, three forms of Cr (VI) anions are present in the solution: $HCrO_4^-$, $Cr_3O_{10}^{2-}$ and $Cr_2O_7^{2-}$, but $HCrO_4^-$ anions predominate. As a result of the electrostatic attraction of $HCrO_4^-$ anions to positively charged amino groups of algae cells, the degree of removal of Cr (VI) ions at pH 1–2 increases. In addition, the authors [31] pay attention to the fact that the size and adsorption energy of the $HCrO_4^-$ ion is smaller than the size and adsorption energy of the
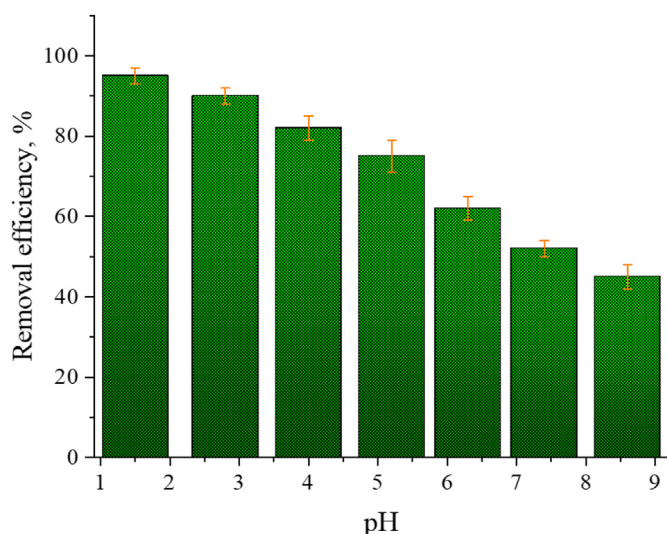
$Cr_2O_7^{2-}$ ion. This contributes to the free penetration of $HCrO_4^-$ ions into the adsorbent layers and an applicable increase in the degree of removal of Cr (VI) ions at pH values 1–2. With an increase in the pH value, $HCrO_4^-$ ions pass into the forms CrO_4^{2-} and $Cr_2O_7^{2-}$ [71]. However, with increasing pH values (pH > pH_{zpc}), the degree of protonation of amino groups of algae decreases and the ionization of acidic groups of the surface increases. Accordingly, the charge on the algae particles becomes negative, which leads to a decrease in the degree of removal due to electrostatic repulsion between the negatively charged surface of the adsorbent and chromium oxyanions.

According to [72], solutions containing Cr (VI) ions at pH = 1 are dominated by H_2CrO_4, which has no charge. Low pH values also accelerate redox reactions in the process, as protons take part in this reaction. The authors [73] determined the zeta potential for two types of algae in the pH range 6–9. While the zeta potential of *Chlorella vulgaris* 13-1 cells was negative at all pH values, *Coelastrella sp.* 3–4 cells show an isoelectric point near pH = 3–4. According to [74], the isoelectric point (pI) of *Chlorella* microalgae is about 3.0, while for *Spirulina* cells pI is 2.8–3.5. In all likelihood, finding the isoelectric point of *Chlorella vulgaris ZBS1* algae cells at pH = 2 (Figure 6) is quite acceptable, since protonation of the amine groups of the surface occurs in a strongly acidic medium, providing a high removal degree of Cr (VI) anions.

At the same time, there is an assumption [75] that the mechanism of Cr (VI) removal by biomaterials is not "anionic adsorption", but "reduction associated with adsorption". Experiments have been developed to obtain data confirming this theory [76]. It was found that the Cr (VI) oxyanion is first adsorbed on positively charged groups of biochar. After that, the reduction of Cr (VI) ions to Cr (III) occurs, which is caused by neighboring electron-donating groups of biosorbents. At the same time, C–O and P–O bonds enriched with electrons act as electron-donating fragments on Cr (VI) ions [77].

When adsorption of Cr (VI) ions on the surface of *Chlorella vulgaris ZBS1* cells in an acidic medium, it is also possible to restore Cr (VI) to Cr (III) by the following reaction (14):

$$HCrO_4^- + 7H^+ + 3e^- \rightarrow Cr^{3+} + 4H_2O \qquad (14)$$
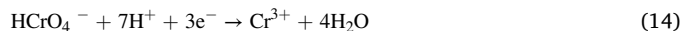
Subsequently, the formed Cr (III) ions can be coordinated with the carboxyl and amine groups of the cell surface [78]. As for the possibility of participation of Cr (III) ions in ion exchange reactions by acid functional groups, this may occur at higher pH values (pH > pH_{zpc}) due to the competition of H^+ ions with Cr (III) cations in an acidic medium.

Thus, during the adsorption of Cr (VI) ions, the functional groups of *Chlorella vulgaris ZBS1* cells can act both as reducing agents and as adsorption sites. Accordingly, a high removal degree of Cr (VI) ions using *Chlorella vulgaris ZBS1* cells in an acidic medium can be carried out both by the mechanism of electrostatic attraction between the amino groups of the surface of algae cells and $HCrO_4^-$ anions. And by the formation of a donor-acceptor bond between the reduced Cr (III) cations and amine, carboxyl groups of the algae surface. The decrease in the degree of removal of Cr (VI) ions in the pH > pH_{zpc} region is justified by the possibility of electrostatic repulsion between the negatively charged surface of the biosorbent and Cr (VI) oxyanions.

Figure 6. Effects of the pH on the degree of removal efficiency (adsorbent dose: 0.125 g/L, C_0: 10^{-3} mol/L, temperature: 298 K).

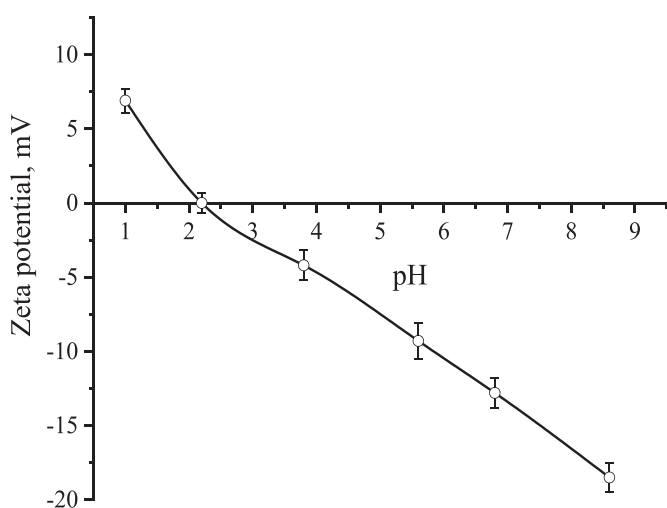### 3.6. FTIR spectroscopic study of the interaction of Chlorella vulgaris ZBS1 algae cells with Cr (VI) ions

The FTIR spectra of *Chlorella vulgaris ZBS1* cells before and after adsorption of Cr (VI) ions at pH = 2 and the initial salt concentration of 10^{-2} mol/L are shown in Figure 8. 8 bands in the range of wave numbers from 450 to 4000 cm^{-1} are clearly distinguished on the FTIR spectrum of the initial algae cells. Peaks at 3448 cm^{-1} indicate the presence of cells on the surface –OH and –COOH groups. CH groups of alkyl chains can cause absorption bands at 2923 cm^{-1}—2852 cm^{-1}. Peaks at 1400 cm^{-1} can be attributed to –COOH groups, and the peak at 1654 cm^{-1} to amine groups of algae proteins [70, 78].
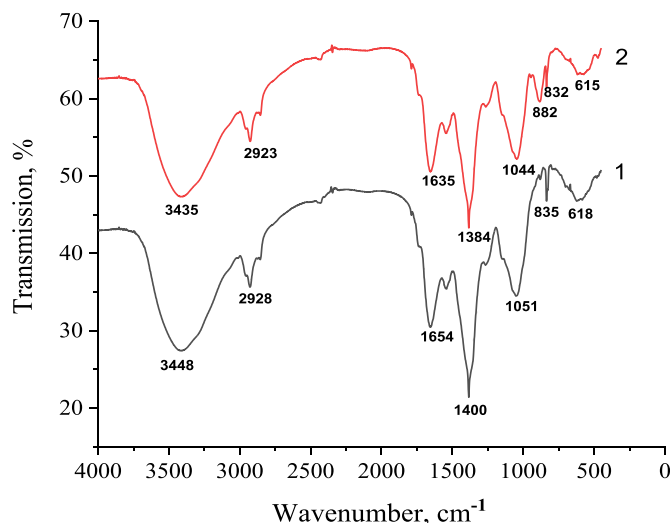

Figure 7. Effect of the pH cells on the zeta potential of the surface of *Chlorella vulgaris ZBS1* algae.

Figure 8. FTIR spectra of the *Chlorella vulgaris ZBS1* algae cells: (1) raw, (2) Cr (VI)-loaded.

Figure 9. Effects of the temperature on the contact time (adsorbent dose: 0.125 g/L, C_0: 10^{-3} mol/L, pH: 8.62).

The peak at an oscillation frequency of 1384 cm^{-1} indicates the presence of C≡N and C=C alkene bonds. The absorption peak at 1051 cm^{-1} can be attributed to C= O and S=O, and the peaks at 835 cm^{-1} can be attributed to sulfate and phosphate groups on the surface of algae cells [48], the peak at 618 cm^{-1} indicates the presence of a strong alkyl halide.

After contact with the K$_2$Cr$_2$O$_7$ solution, a significant shift in the peaks of the FTIR spectrum was observed. The peak at 3448 cm^{-1} was shifted to 3435 cm^{-1}, which indicates the interaction of hydroxyl and carboxyl groups of algae compounds with Cr (VI) ions. Note that the study was conducted at pH = 2, therefore, the interaction of these functional groups of algae with Cr (III) ions can be assumed. At the same time, the peak at 1654 cm^{-1} is shifted to 1635 cm^{-1}, this is due to the complexation of amino groups with reduced Cr (III) ions. The peaks at 1051 cm^{-1} and 835 cm^{-1} also underwent significant changes, which indicates the participation of phosphate and sulfate groups in the binding of metal ions. The peak at 882 cm^{-1} corresponds to Cr–O or Cr = O vibration, which indicates the attachment of chromium ions from the solution to the surface of *Chlorella vulgaris* algae cells [79].

The results of FTIR spectroscopy indicate the presence of various functional groups on the surface of *Chlorella vulgaris ZBS1* algae cells: phosphate, carboxyl, sulfide, sulfate, amine, hydroxyl, etc. The shift of the peaks corresponding to these groups indicates their interaction with Cr (VI) ions, which can be restored to Cr (III) during contact with cells. As for the mechanism of interaction of these groups with Cr (VI) ions and reduced Cr (III) ions, it can be carried out due to ion exchange, electrostatic attraction and donor-acceptor coupling.

3.7. Thermodynamic research

3.7.1. Effect of temperature on the adsorption of Cr (VI)

The effect of temperature on the adsorption of Cr (VI) ions on the surface of *Chlorella vulgaris ZBS1* cells at pH = 8.62 was studied at four different temperatures: 298, 308, 318 and 328 K. As shown in Figure 9, with an increase in temperature from 298 to 328 K, the adsorption value increased. This means that Cr (VI) ions have become more active in reacting with algae cells.

According to data [3], with an increase in temperature, the adsorption of Cr (VI) ions on the surface of *S. oligocystum* cells decreases, which is explained by the shrinkage of the adsorbent, leading to a decrease in the contact of its active centers with the salt solution. In the case of the *Chlorella vulgaris ZBS1* system, it should be taken into account that under experimental conditions the pH of the medium is 8.62. Under these conditions, both the surface of the adsorbent and the Cr (VI) ions are
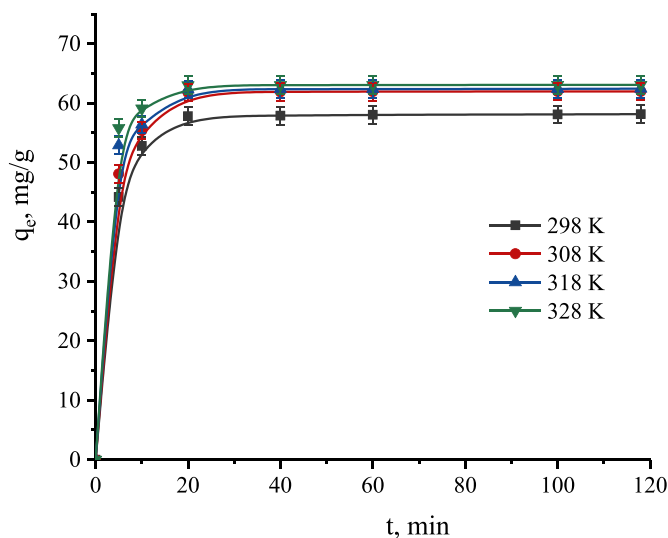
negatively charged, therefore, electrostatic repulsion forces act between them, preventing adsorption. An increase in temperature here also leads to shrinkage of the adsorbent, however, shrinkage reduces the availability of negatively charged groups on its surface involved in the electrostatic repulsion of Cr (VI) oxyanions. As a result, the adsorption value increases with increasing temperature.

Experimental data on the adsorption of Cr (VI) ions at different temperatures were processed using the pseudo-first (PFOM), pseudo-second (PSOM) order equations, the kinetic model of intraparticle diffusion (IPDM) and the Elovich model (ELM) (Figure 10(a, b, c. d)). As can be seen from Table 3, in the temperature range of 298–328 K, the correlation coefficient (R^2) of PFOM and PSOM for Cr (VI) adsorption was determined in the range of 0.8583–0.9702 and 0.9997–0.9998, respectively (Figure 10(a, b)). PFOM is not suitable for describing the kinetic behavior of the adsorption process, since the value of $q_{e.cal}$ for the adsorption of Cr (VI) ions is much lower than $q_{e.exp}$. The correlation coefficient (R^2) for PSOM is 0.9997 and higher than in the case of PFOM, IPDM and ELM. This shows that the adsorption of Cr (VI) ions on the surface of *Chlorella vulgaris ZBS1* algae cells can be described as a pseudo-second order process. In addition, the difference between $q_{e.cal}$ and $q_{e.exp}$ in PSOM is much smaller than in other studied models, which confirms that the adsorption data correspond to a pseudo-second order. The k_2 values in PSOM increase with increasing solution temperature, this is due to an increase in adsorption due to a decrease in the electrostatic repulsion of Cr (VI) anions from a negatively charged surface due to blocking of anionic functional groups of algae during shrinkage of the biosorbent. Whereas in PFOM the change in k_1 values does not have such a pronounced trend. However, although PSOM is able to describe the kinetic behavior of the process, this model does not provide information about the limiting rate of phase transition in the algae cell system—Cr (VI) ions. Consequently, the limiting step velocity may be related to the stage of penetration of Cr (VI) ions into particles or into the liquid film of cells [31].

IPDM was used to determine the step size limit. The high C_i value in Table 4 indicates a high effect of boundary layers in the process of adsorption of Cr (VI) ions. With an increase in the temperature of the solution, the thickness of the adsorbent boundary layer increases, but does not equal the values of q_{e2} in PSOM. The graph of the kinetic model of intraparticle diffusion is not linear (Figure 10(c)), however, with increasing temperature, the constant of intraparticle diffusion of Cr (VI) ions decreases, which is associated with increased hydrophobic interactions between nonpolar sites of protein macromolecules and polysaccharides in the composition of algae cells. This conclusion indicates
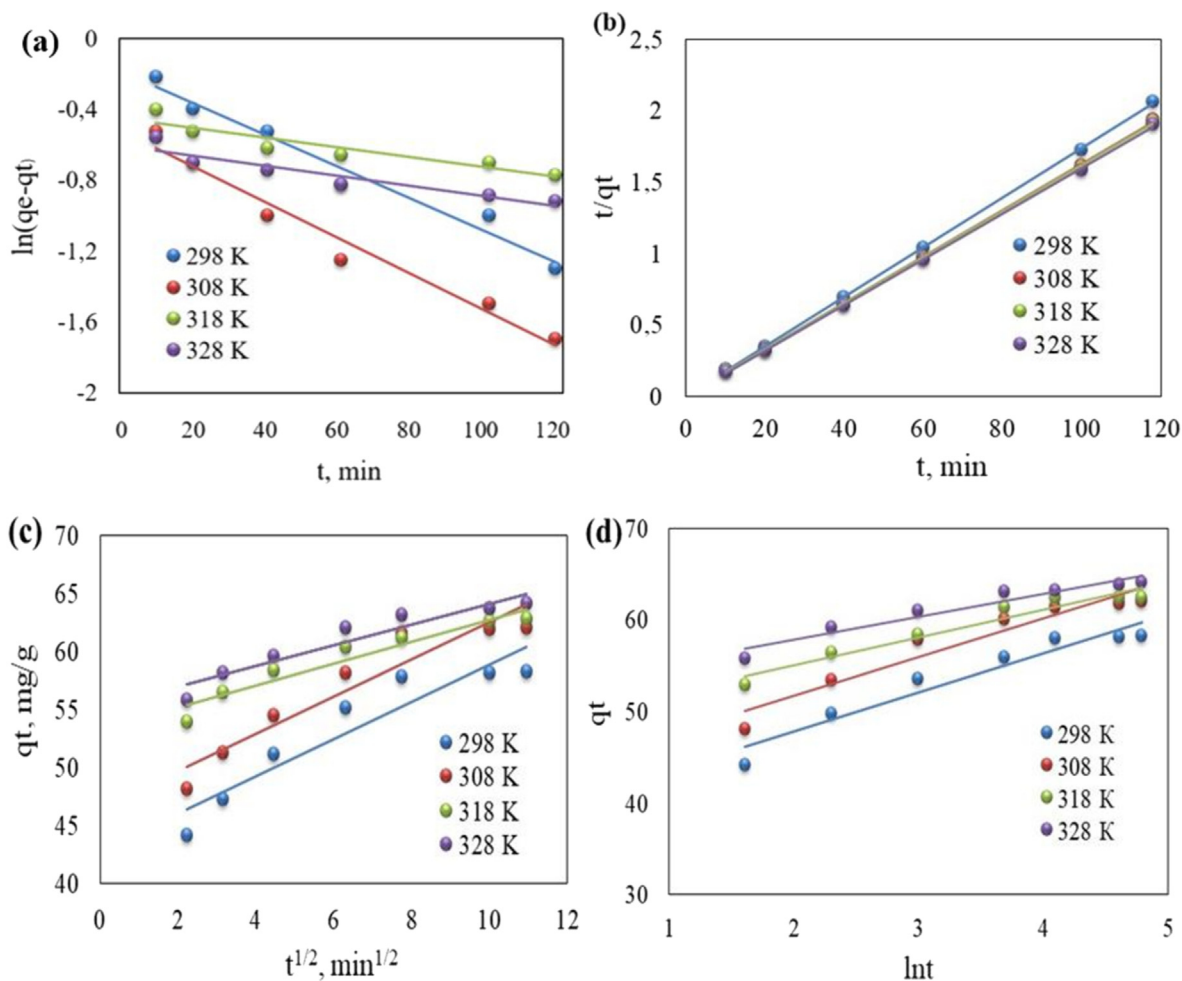
Figure 10. Kinetics plots of (a) PFOM, (b) PSOM, (c) IPDM and (d) ELM.

Table 3. Kinetic parameters of Cr(VI) ions adsorption on the surface of *Chlorella vulgaris ZBS1* algae.

Temperature (K)	Experimental data q_e (mg/g)	PFOM			PSOM		
		$q_{e1.cal}$ (mg/g)	k_1 (1/min)	R^2	$q_{e2.cal}$ (mg/g)	k_2 ((g/min)/mg)	R^2
298	58.15 ± 1.5	0.67	0.02	0.9702	57.80	0.1	0.9997
308	61.98 ± 1.5	0.31	0.02	0.9697	61.72	0.1	0.9997
318	62.43 ± 1.5	0.36	0.01	0.8583	62.11	0.13	0.9997
328	63.08 ± 1.5	0.25	0.01	0.8857	62.50	0.23	0.9998

Table 4. Kinetic parameters for IPDM and ELM.

Temperature (K)	IPDM			ELM		
	k_{dif} (mg/g ·min$^{0.5}$)	C_i (mg/g)	R^2	α (mg/g·min)	β (g/mg)	R^2
298	1.603	42.817	0.8806	9.136	0.233	0.9319
308	1.595	46.523	0.9032	10.231	0.237	0.9208
318	0.949	53.254	0.9222	16.176	0.329	0.9401
328	0.898	55.131	0.9104	21.346	0.4	0.9369

that, in addition to other characteristics of algae, electrostatic repulsion between Cr (VI) ions and the surface of *Chlorella vulgaris ZBS1* cells can also affect the rate of adsorption [80].

Another kinetic model used to describe the adsorption behavior of heavy metals is the Elovich model (ELM) (Figure 10(d)). The Elovich

model assumes that the active centers of the adsorbent are heterogeneous, this may mean that the adsorbents have a poorly ordered structure, and their surface is heterogeneous, and therefore has different adsorption energy [31, 32], which is not surprising in the case of a biosorbent with different functional groups. With an increase in temperature to 328 K, the values of the α and β constants became quite high: 21.346 g/mg min and 0.4 g/mg, respectively. Such values of α and β relate to the degree of surface coverage and activation energy for chemisorption [48]. This model takes into account the contribution of both the adsorption process and the desorption phenomenon to the kinetics of substance extraction, which acquires a significant effect on adsorption when approaching the equilibrium state. In general, the data obtained indicate that chemical adsorption may also take part in the extraction of Cr (VI) ions in addition to physical adsorption. In this case, for the adsorption of Cr (VI) ions on *Chlorella vulgaris ZBS1* cells, both the state of metal ions and the state of functional groups of algae cells, as well as the recovery

processes taking place with the participation of functional groups, will be decisive.

3.7.2. Effect of temperature on thermodynamic parameters of adsorption of Cr (VI) ions

To study the thermodynamics of adsorption of Cr (VI) ions on the surface of *Chlorella vulgaris ZBS1* cells, thermodynamic constants such as changes in enthalpy ΔH, free energy ΔG and entropy ΔS were calculated. The following equations were used for the calculation [24, 25, 26, 27, 28, 29, 30, 31, 32, 33,44,53] (15, 16, 17):

$$\Delta G^0 = -RT \ln k_D \tag{15}$$

$$k_D = \frac{q_e}{C_e} \tag{16}$$

$$\ln k = \frac{-\Delta G^0}{RT} = \frac{-\Delta H^0}{RT} + \frac{\Delta S^0}{RT} \tag{17}$$

where q_e is the fraction of Cr (VI) ions adsorbed at equilibrium, and T is the temperature in K.

According to Figure 11, the data of Table 5 are calculated. As can be seen from Table 5, the enthalpy change ΔH is positive, that is, the process is endothermic due to an increase in adsorption with increasing temperature. Usually, large enthalpy changes (>60 kJ/mol) are observed during chemical adsorption, while physical adsorption is accompanied by heat of less than 40 kJ/mol [41, 56]. The low value of ΔH, equal to 6.65 kJ/mol, shows that the adsorption process is mainly due to physical interactions.

A positive value of ΔG gives reason to assume that the adsorption of Cr (VI) at different temperatures is not by nature a spontaneous process. Usually, the Gibbs free energy for physical adsorption is 0–20 kJ/mol [81, 82] and the values of ΔG for the adsorption of Cr (VI) ions are included in this interval. A positive value of ΔS indicates the randomness of the adsorption process at the algae–solution cell boundary, which may be due to a large variety of functional groups capable of binding Cr (VI) ions. In addition, at all temperatures, the condition ΔH > TΔS is fulfilled, indicating that the adsorption of Cr (VI) ions on the surface of *Chlorella vulgaris ZBS1* cells is dominated by a change in enthalpy, not entropy. All this highlights the decisive role of non-covalent electrostatic interactions in the adsorption of Cr (VI) ions on the surface of *Chlorella vulgaris ZBS1* algae cells. The reason for the endothermicity and spontaneity of the adsorption process, namely the positive sign of ΔH and ΔG, is the expenditure of energy to suppress electrostatic repulsion between the
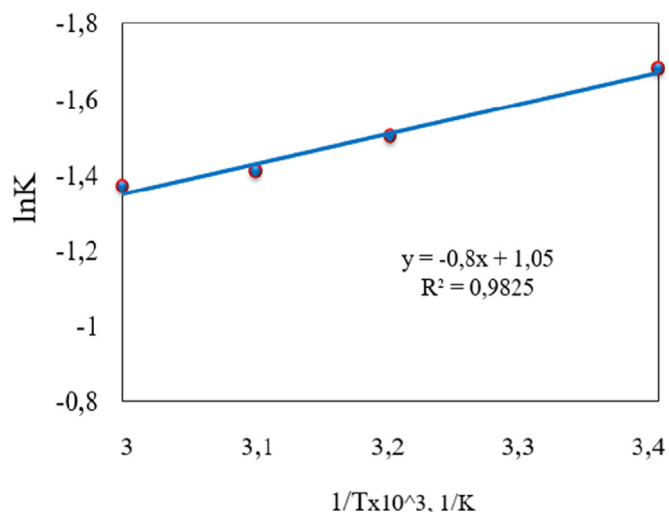

Figure 11. Dependence of lnK on 1/T for thermodynamic parameters calculation.

Table 5. Thermodynamic parameters of adsorption of Cr (VI) ions on the surface of *Chlorella vulgaris ZBS1* algae cells.

Cr (VI)	ΔH (kJ/mol)	ΔS (J/mol)	ΔG (kJ/mol)			
			298 K	308 K	318 K	328 K
	6.65 ± 0.25	8.72 ± 0.2	4.18 ± 0.2	3.68 ± 0.1	3.73 ± 0.1	3.75 ± 0.2

anionic groups of the surface of algae cells and Cr (VI) anions, which is achieved when algae cells shrink due to heating of the system.

As for the selectivity of the adsorption of Cr (VI) ions on the surface of *Chlorella vulgaris ZBS1* algae cells, this requires a separate study. Regarding the regenerability of the biosorbent, it should be noted that according to [72, 83, 84] biosorbents based on cells of the *Spirulina platensis Detarium senegalense, Turbinaria conoides* and *Sargassum wightii* withstand from 5 to 10 cycles of reuse.

Thus, *Chlorella vulgaris ZBS1* algae cells are effective and economical adsorbents for removing Cr (VI), which not only bind them, but also have a regenerating effect on them and this can be a solution to the problem of waste water treatment for Cr (VI) industries. However, for the use of algae cells in water purification, further research is needed to determine their overall environmental impact. When describing the mechanism of interaction of Cr (VI) ions with functional groups of algae cells, it is necessary to take into account the state of Cr (VI) ions, which is largely determined by the pH values of the medium.

4. Conclusion

1. Adsorption of Cr (VI) ions on the surface of *Chlorella vulgaris ZBS1* algae cells was investigated. The adsorption data were processed within the framework of Langmuir, Freundlich, Dubinin-Radushkevich and Temkin models. It is shown that the maximum Langmuir adsorption value is 74.63 mg/g. The values of the parameters $1/n$ and K_f in the Freundlich model were determined as 0.713 and 2.82 mg/g, respectively, which indicates the favorability of adsorption. The low values of the free energy of the adsorption process—2.604 kJ/mol according to the Dubinin-Radushkevich model and 18.215 kJ/mol according to the Temkin model—indicate the predominantly physical nature of adsorption.

2. Acidification of the medium leads to an increase in the removal degree of Cr (VI) ions and reaches 94.6–95.4% in the pH range 1–2. This is justified, on the one hand, by the electrostatic attraction of $HCrO_4^-$ groups to protonated amino groups of the cell surface. On the other hand, in an acidic environment, it is possible to restore Cr (VI) ions to Cr (III) ions, which can form coordination bonds with amine and carboxyl groups of algae cells.

3. It was found that an increase in the concentration of the Cr (VI) salt solution from 10^{-5} mol/L to 10^{-4} mol/L leads to an increase in the negative values of the zeta potential of *Chlorella vulgaris ZBS1* cells from −12.5 mV to −22.1 mV. However, a further increase in the concentration of $K_2Cr_2O_7$ causes a decrease in the negative values of the zeta potential, which is justified by the accumulation of ions in the solution K^+, neutralizing the charge of anionic functional groups.

4. According to FTIR spectroscopy data, the participation of phosphate, sulfate, carboxyl and amine groups of algae in the binding of Cr (VI) ions is justified, which can be carried out due to electrostatic attraction, ion exchange and donor-acceptor interaction.

5. The study of adsorption kinetics has shown, that the adsorption of Cr (VI) ions on the surface of *Chlorella vulgaris ZBS1* algae cells is described in the framework of the pseudo-second order model. An increase in temperature leads to an increase for adsorption, which is associated with a decrease in electrostatic repulsion between Cr (VI) anions and the negatively charged surface of algae cells, due to increased hydrophobic interactions between nonpolar sites of protein macromolecules and polysaccharides in the cells.

6. Calculation of thermodynamic parameters of adsorption of Cr (VI) ions on the surface of *Chlorella vulgaris ZBS1* algae cells showed, that adsorption is an endothermic and non-spontaneous process. This is justified by the expenditure of energy to suppress the electrostatic repulsion between the anionic groups of the surface of algae cells and Cr (VI) anions, which is achieved during shrinkage of algae cells by increasing the temperature of the system.

Declarations

Author contribution statement

Zhadra Tattibayeva: Performed the experiments; Contributed reagents, materials, analysis tools or data; Analyzed and interpreted the data; Wrote the paper. Sagdat Tazhibayeva: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper. Wojciech Kujawski: Conceived and designed the experiments. Bolatkhan Zayadan, Kuanyshbek Musabekov: Contributed reagents, materials, analysis tools or data.

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Data availability statement

Data included in article/supplementary material/referenced in article.

Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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