

Article

Development of Full-Cycle Utilization of *Chlorella sorokiniana* Microalgae Biomass for Environmental and Food Purposes

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Abstract: The application of microalgae biomass of *Chlorella sorokiniana* as environmentally friendly biosorbents for removing potentially toxic elements (PTE) from water and as a source of biofuel has been thoroughly studied. In this paper, we investigate its physicochemical properties (infrared spectroscopy (IR spectra), microstructure, adsorption properties); we have managed to isolate the lipid complex, which amounted to 20% of dry biomass. Studies of the lipid complex showed that 80.02% of lipids are unsaturated fatty acids (C18:1, C18:2, C18:3). Additionally, we have investigated the efficiency of using the residual biomass obtained after lipid extraction for water purification from rare-earth metals (REM) and PTE. To increase the sorption properties of residual biomass, its thermal modification was carried out and sorption materials based on heat-treated residual biomass and chitosan were created. The physicochemical and mechanical properties of the obtained sorption materials were studied. The total sorption capacity was 31.9 mg/g for REM and 349.7 mg/g for PTE. Moreover, we propose a new method for the disposal of spent sorbents as additional fuel. Spent sorbents can be considered to be biofuel in terms of energy content (20.7 MJ*kg⁻¹). The results of this study provide the basis for increased use of microalgae.

Keywords: microalgae; sorbents; water purification; REM; PTE; lipids; Omega-3; biofuel

1. Introduction

Sustainable biomass-based fuels produced through transesterification [1,2], anaerobic digestion and fermentation [3–7], extraction [8,9], hydrothermal carbonization [10–13], pyrolysis [14–19], gasification [20–23], liquefaction processes [24–26] are excellent alternative fuels and can play an important role in reducing the formation of greenhouse gases and acid rain.

Over the past decade, many researchers have proposed algae and microalgae as raw materials for biofuel production, however, their use is associated with a number of problems, mainly due to the high water content in algae and microalgae [27]. As microalgae have rather distinct properties in comparison with other biomass types and such differences have a more positive eco-technology impact during the

utilization of microalgae and their conversion products, simultaneously producing biomaterials and products for bio-remediation seems to be a promising avenue [28–30]. Numerous reviews of utilization of algae and microalgae in biorefinery concepts are available [31,32]. Nowadays, microalgae are widely used in a variety of ways. Having rich vitamin and protein composition, microalgae are utilized for livestock feed and even as human food [33–36]. The authors in the articles [37–39] described various applications of microalgae for medical and environmental purposes. An interesting scientific approach is obtaining a variety of valuable components from microalgae, namely:

1. Lipids, which, depending on the fatty acid composition, can be sources of Omega-3, Omega-6 [40] or biofuel;
2. Biosorbents for metal biominer; and
3. Enterosorbents for detoxification.

Ways and methods for obtaining lipids from algae have been studied by scientists around the world. American scientists [41] have investigated three strains of *C. sorokiniana* species and developed a lipid extraction technique. Chader et al. [42,43] cultivated *Chlorella* for subsequent production of biofuels. Its biomass was centrifuged, dried to constant weight, and lyophilized. The gas chromatographic method was used to determine the composition of fatty acids. The results showed that a mixture of unsaturated fatty acids consisted of oleic (18:1), linoleic (18:2) and linolenic (18:3) acids; saturated fatty acids, namely, palmitic (16:0) and stearic (18:0), were also present to a small extent. Palmitic, stearic, oleic and linoleic acids are the most common fatty acids contained in biodiesel. In laboratory conditions, Blinová [10] obtained biofuel for diesel engines from *C. Vulgaris*. The influence of growth conditions on the properties of biodiesel was evaluated, and the properties of the resulting biofuels were found to comply with ASTM (American Society for Testing and Materials) standards.

At the same time, growing global demand for rare-earth metals (REM) has led to a shortage of primary resources. Nowadays, traditional REM extraction processes are energy-consuming and not environmentally friendly due to the use of various toxic chemicals.

REM and potentially toxic elements (PTE) are used in various industries. Obtaining REM materials from secondary (waste) instead of from primary (natural) resources is of great current interest. The problem of wastewater treatment with regard to PTE and REM is relevant worldwide [44]. The main sources of these contaminations are waste from mining and processing enterprises and effluents from industrial companies, chiefly metal processing. Biominer is a new technology that uses biological systems to extract metals from liquid media. This technology has been studied until now only for copper, nickel and gold. Biochemical mechanisms, including biominer of primary minerals, are used in articles [45,46]. Studies on the recovery of metals from secondary sources using the concept of biominer have not yet been widely conducted. It can be applied to processing wastewater and discarded electronic equipment [47].

Sorption mechanisms include the use of dead biomass [48]. In this case, dead biomass is more flexible to environmental conditions and to various concentrations of most pollutants, including PTE and REM. Various sources of biosorbents, such as bacteria, yeast, fungi, algae, and plant biomass, can be used for sorption of metals [49]. As a rule, various biomaterials have biosorption potential for sorption of various metal ions. In preliminary works presented in articles [50,51], *C. Vulgaris* green microalgae were studied as a potential biosorbent for extracting neodymium from its magnetic filtrates in batch and continuous sorption systems. High metal biosorption by microalgae biomass has been achieved by some scientists [50,51], showing the concept of sorption processes and the absorption mechanism. Some functional groups have been found in algae cells that initiate the binding of metals, such as hydroxyl, carboxylate, and amino groups.

Besides *C. Vulgaris*, *C. Sorokiniana* is widely used for metal extraction. Sorption of PTE (copper, nickel, cadmium) from drinking water by *C. Sorokiniana*, immobilized on an extract from *Laminaria* algae was studied in articles [52]. The sorption process was studied in the range of initial concentrations 5–350 mg/l and the pH was 3–7.

In the article [53], *C. Sorokiniana* cells immobilized in loofa sponge were used to extract chromium ions. A loofa sponge was prepared by boiling in distilled water, followed by washing. The introduction of microalgae was carried out within 24 days. Subsequently, the samples were used to extract chromium ions from model solutions. The extraction efficiency for chromium (III) ions was 98%, the sorption capacity was 69.9 mg/g. The possibility of its reuse, at least for 5 cycles, is proven. Thanks to the ease of use, the problem of the possibility of using biosorbent on an industrial scale has been solved.

The processes of chromium (III) sorption using green algae were studied by the authors of [54]. The metal removal was carried out using specially prepared granules with a diameter of several millimetres, which consisted of a polymer base and some powder of *C. Vulgaris* or *S. Acutus* included in it.

Representatives of the genus *Chlorella* often enter into symbiotic relationships with various fungi species. In the article [55], the microalga *C. Vulgaris* UMN235 and two locally isolated species of fungi *Aspergillus* sp. UMN F01 and UMN F02 were used to study the influence of various conditions on the granulation of the mushroom–algal complex. The results showed that pH is the key factor affecting granule formation, and it can be controlled by changing glucose concentration and adding fungal spores. The obtained technology allows for simplifying the algae harvesting process and increasing wastewater treatment efficiency.

It is not economically viable to use the original microalgae biomass, because it contains a large amount of fatty acids, which are part of biofuels and Omega-3.

The authors hypothesize the possibility of cascading the use of microalgae for environmental and food purposes, at the first stage isolating lipid fractions for biofuel and Omega-3, and at the second stage using residual biomass as sorbents for water purification from REM and PTE.

2. Materials and Methods

2.1. Cultivation of Microalgae Biomass

To obtain the microalgae biomass, we used 8 closed photobioreactors with a volume of 30 litres each (Figure 1a), which allowed us to cultivate biomass in natural conditions, and a closed photobioreactor with a volume of 90 litres (Figure 1b,c) for laboratory conditions.

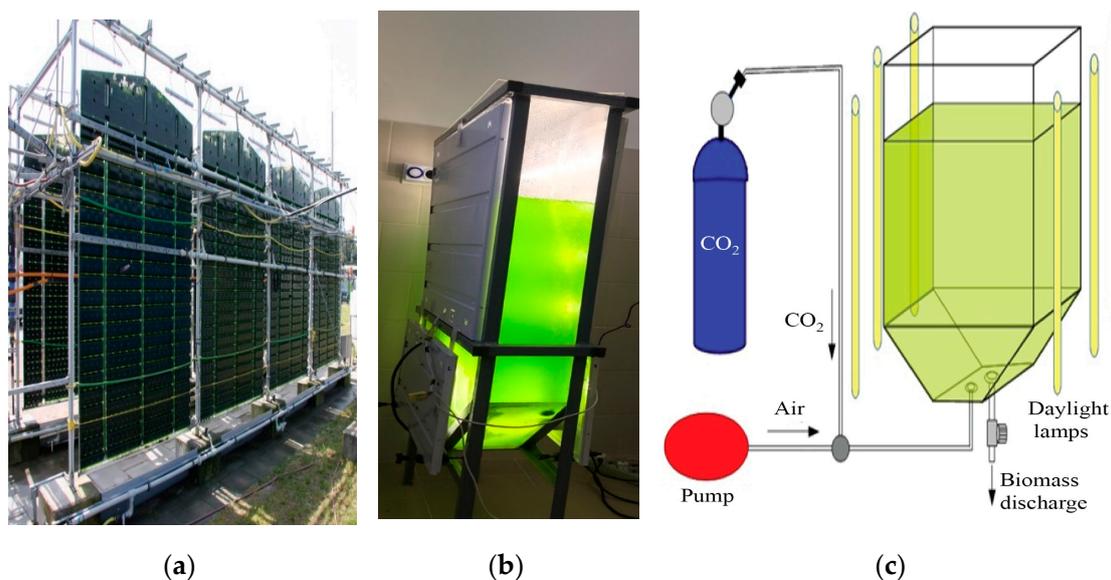


Figure 1. Closed photobioreactors for *C. Sorokiniana* microalgae biomass cultivation: (a) for cultivation under natural conditions, (b) for cultivation under laboratory conditions, (c) photobioreactor scheme.

To obtain biomass from growth of microalgae, *C. Sorokiniana* was cultivated, concentrated and dried. To obtain the maximum amount of *C. Sorokiniana* biomass in our laboratory, the following conditions were maintained: pH = 8.0 ± 0.5 ; light intensity of 2500 ± 300 Lx; temperature of 28 ± 2 °C; aeration not less than 1.5 l/min and the cultivation time of 10 days.

Biomass growth was monitored by optical density using a spectrophotometer Shimadzu UV- 1208. Cell counting was performed using a Goryev's camera. Under natural conditions, it is rational to cultivate algae from mid-April to mid-October, i.e., the cultivation period is 6 months per year.

2.2. Obtaining Dry Biomass

For lipid extraction processes, it is necessary to use dry microalgae biomass. For this, microalgae suspension was concentrated and dried.

Concentrations were carried out using a 12 L centrifuge, Avanti J-30i Beckman Coulter, with a cooling system. Centrifugation speed was 30,000 rpm. The resulting thick paste (moisture content up to 40%) was dried by the lyophilic method, within which the paste was first frozen at $T = -20$ °C and then lyophilized at a pressure of 1 mbar (-20 °C) at an ice condenser temperature of -55 °C using the Alpha 1-2 LDplus lyophilization device from Martin Christ Gefriertrocknungsanlagen GmbH.

2.3. Determination of Specific Surface Area

The specific surface area of materials was determined by low-temperature nitrogen adsorption (-196 °C) using the BET (Brunauer, Emmett and Teller) method on the TriStar II 3020 automated sorption installation from Micromeritics (USA). The volumetric version of the sorption method was used.

2.4. IR Spectra

The IR spectra of the residual biomass and sorbents were recorded using the FSM 1201 spectrometer. A KBr tablet obtained by pressing its crystalline powder during vacuum pumping was used as a reference sample. Samples were obtained by pressing a mixture of the test powder (5 mg) and KBr. The total weight of the tablet with the test sample was 300 mg.

2.5. Lipid Extraction and Determination of Their Composition

The lipid fraction extraction from *C. sorokiniana* microalgae biomass was carried out on the Büchi E-812 SOX Soxhlet apparatus. For this, 3 g of dry biomass was placed in a cellulose glass (33 mm × 94 mm). A mixture of ethanol and n-hexane (1:9), was used as an extractant. For 3 g of dry biomass, 100 ml of extractant was used. We studied and established the optimal extraction parameters for the maximum lipid yield (20%): the extraction time of 3.5 hours; hexane and ethanol (9:1) used as an extractant; 10 cycles of extraction. The qualitative composition of total lipids obtained from the biomass of *C. Sorokiniana* microalgae was investigated by thin layer chromatography (TLC) using PTCX-AF-B plates. Plate analysis was performed using the Sorbfil densitometer and Sorbfil TLC software (Version 1.0, Sorbpolimer, Krasnodar, Russia). For this, lipid samples obtained from *C. Sorokiniana* microalgae in the amount of 3 µl were deposited to PTSX-AF-B chromatographic plates. The plate was placed in a chromatographic chamber, which was prefilled with a mixture of solvents: petroleum ether/diethyl ether/acetic acid in a ratio of 90:10:1. The plate was immersed in a solvent to the depth of 5–6 mm. The distillation was carried out for 50–60 minutes at room temperature. After this, the plate was dried and sprayed with a 30% sulfuric acid solution. Sprayed plates were kept in an oven heated to a temperature of 180 °C for 30 minutes. As a result, all lipids were charred and formed black spots. After the development of the analyzed plate, it was placed in a lighting chamber, for this it was fixed on a stage, introduced into the chamber, and illuminated with light of a selected wavelength. The plate image was stored in the computer memory using a Sony video camera; the video image was processed using the Sorbfil TLS View program. Compounds were identified using reference data on the path length.

The composition of higher fatty acids in the lipids obtained from the *C. Sorokiniana* microalgae biomass was determined using the gas chromatograph with a flame ionization detector Agilent technologies sales and services GmbH and Co.KG, on a BPX70 column (60 m × 0.25 mm × 0.25 μm), SGE analytical science, VWR international GmbH; carrier gas was nitrogen.

2.6. Microstructural Studies

Microstructural studies were performed using scanning electron microscopy at JSM-7001F, Jeol.

2.7. Obtaining Sorbents and Studying Their Sorption Properties

The scheme for producing adsorbents is shown in Figure 2.

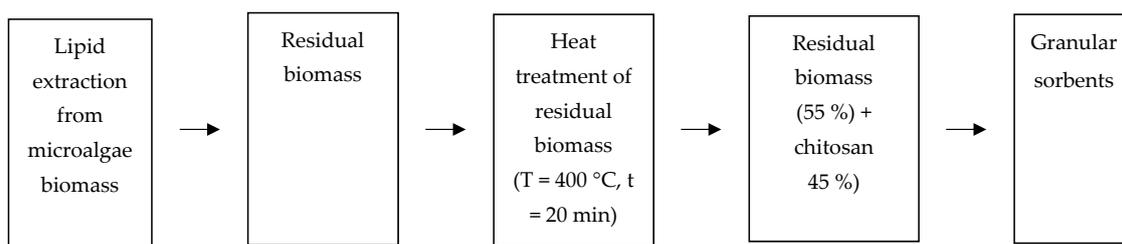


Figure 2. Experiment design.

The residual biomass was thermally treated at $T = 400\text{ °C}$ for 20 min in a special cell without oxygen. The obtained heat-treated residual biomass was a fine black powder. Granules were made from heat-treated powder of residual biomass by droplet granulation; the procedure is described in detail in articles [56–58]. Chitosan, which is a safe biodegradable biopolymer, was used as a binder, therefore not harming the environment. The composition of the mixture and dry granules of experimental samples of sorption material from the residual biomass of microalgae *Chlorella sorokiniana* is 5:95 mass % for the mixture and 55.5:44.5 wt. % for dry granules. Sorption properties of sorbents made of residual biomass were investigated under the conditions: ratio of sorbent mass and solution = 2 g per 1 dm³; pH = 4.0 ± 0.2 units of pH; $T = 293 \pm 2$ K. The sorption process was carried out in two stages, initially the solution with a weighed portion of the sorbent was mixed in the OS-20 laboratory shaker from Biosan (Latvia) for 2 hours at a velocity of $v = 250$ rpm. For the remaining time (22 hours), the solution was static. The required pH value was adjusted with HNO₃ (7%) and NaOH (7%) solutions and controlled using a laboratory ion meter I-160MI (LLC "Measuring technique"). We used model solutions containing Zn (II), Cd (II), Cu (II) ions, which were prepared from CuSO₄·5H₂O, ZnSO₄·7H₂O and 3CdSO₄·8H₂O salts, and for the preparation of model solutions of REM we have used standard samples. The initial concentration of the solutions was 50 mg/g. At the end of the sorption process, the sorbent mass was separated from the solution by filtration using a decalcified White Ribbon filter, and the solution was decanted after purification with sorbents. The initial and equilibrium solution concentration before and after treatment with sorbents were evaluated using the inversion voltammetry on a TA-Lab analyzer (NPP Tomanalit, Tomsk, Russia).

Studies on the extraction of REM from model solutions with various concentrations were carried out at pH = 4. Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) was used to determine the concentrations in the REM solution.

The efficiency (E) of model wastewater purification was calculated according to the formula:

$$E = \frac{C_0 - C_t}{C_0} \cdot 100\%, \quad (1)$$

where C_0 and C_t are initial and final concentration of solution, mg/l.

The adsorption capacity A_i of adsorbent at any given time was determined by the equation:

$$A_i = \frac{C_0 - C_t}{m} V . \quad (2)$$

where C_0 is the initial concentration, C_t is the solution concentration at a given time, g/l; m is the sorbent mass, g; V is the solution volume, L.

2.8. Determination of Specific Heat of Combustion

Tests for determining the higher heating value (HHV) of the spent sorbents were carried out at the laboratory of the Hamburg University of Technology (Germany) using the IKA C 5000 calorimeter. The device used is a bomb calorimeter with an adiabatic jacket in accordance with DIN EN 51900-3. The spent sorbents are predried at 45 °C to constant weight, then crushed to <0.25 mm. The lower heating value LHV is calculated from the HHV.

3. Results

Our results show that over 10 days of cultivation, the biomass reached an optical density of 1.7, which corresponds to 43×10^6 cells/ml. When growing biomass of microalgae in a volume of 90 L, it is possible to obtain about 54 g of dry biomass.

Investigations showed that centrifugation, i.e., separation due to centrifugal forces is the best way of concentrating. It facilitates removal of the maximum amount of liquid from the microalgae biomass. The resulting thick paste was lyophilized, as this type of drying allowed us to obtain biomass with dry porous structure, Figure 3.

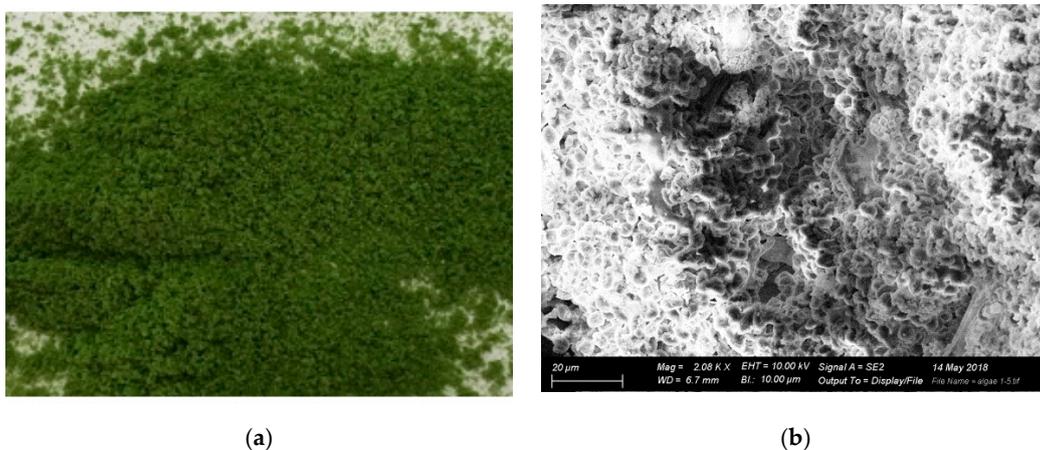


Figure 3. Surface microstructure of *C. sorokiniana* biomass after lyophilization: (a) external view; (b) microstructure.

To determine the presence of functional groups, the IR spectra of the obtained microalgae biomass were recorded (Figure 4).

Table 1 describes the characteristics of the spectrum.

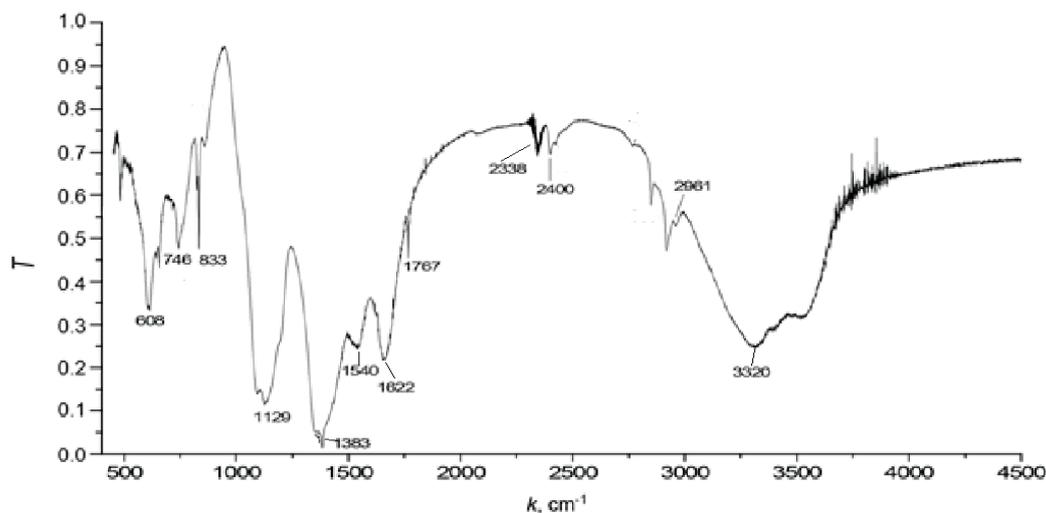


Figure 4. IR spectra of *C. sorokiniana* biomass.

Table 1. Spectral characteristic of *C. sorokiniana* biomass [59].

Wavelength, cm^{-1}	Functional Groups
1000–1100	Oxygen-containing C-O bond groups
1300–1400	Deformation vibration of NH-groups
1600	Carboxyl groups C=O,
2800–2900	Asymmetric bonds of CH_2 groups
3100–3600	Valence vibrations of OH groups

A wide peak at 3100–3600 cm^{-1} was detected, which can be considered belonging to a hydroxyl (O–H) group, responsible for the formation of hydrogen bonds. Peaks in the 2800–2900 cm^{-1} range are due to asymmetric stretching of CH_2 groups of alkanes. The peak at 1622 cm^{-1} can be attributed to the C=O carboxy stretching, which can correspond to various acids, aldehydes and ketones, which are usually formed during the degradation of cellulose and hemicellulose. A relatively sharp peak at 1000–1100 cm^{-1} is governed by C–O stretching of various oxygen-containing compounds. The presence of the detected groups in the obtained biomass suggests the possibility of a chemisorption mechanism for the extraction of PTE from solutions, due to cation exchange according to the scheme: $z\text{R}\cdot\text{OH} + \text{Me} + z = z\text{R}\cdot\text{OMe} + z\text{H}_2\text{O}$.

The resulting biomass, i.e., biosorbent, was investigated for the ability to sorb PTE from model wastewater. We have constructed adsorption isotherms of PTE (Cu (II), Cd (II), Zn (II)) by biosorbents (microalgae biomass) and calculated respective maximum sorption capacities. The maximum sorption capacity (A , mg/g) was determined, which decreases in the following order: Cu (II) 54.2 < Cd (II) 88.7 < Zn (II) 98.5. From the obtained data we can see that the microalgae biomass has high sorption properties and can be used as a biosorbent.

It is known from [41] that microalgae contain a large amount of fatty acids and act as sources of biofuel and Omega-3. We proposed to obtain not only lipids for Omega-3 and biodiesel, but also to use residual biomass to obtain sorbents for water purification from PTE and REM.

The obtained lipids from the biomass of *C. Sorokiniana* were studied by thin-layer chromatography based on the chromatographic mobility of substances R_f , identified in Figure 5:

- Sterols $R_f = 0.19$;
- Fatty acids $R_f = 0.39$;
- Triglycerides $R_f = 0.60$;
- Long-chain aldehydes $R_f = 0.73$.

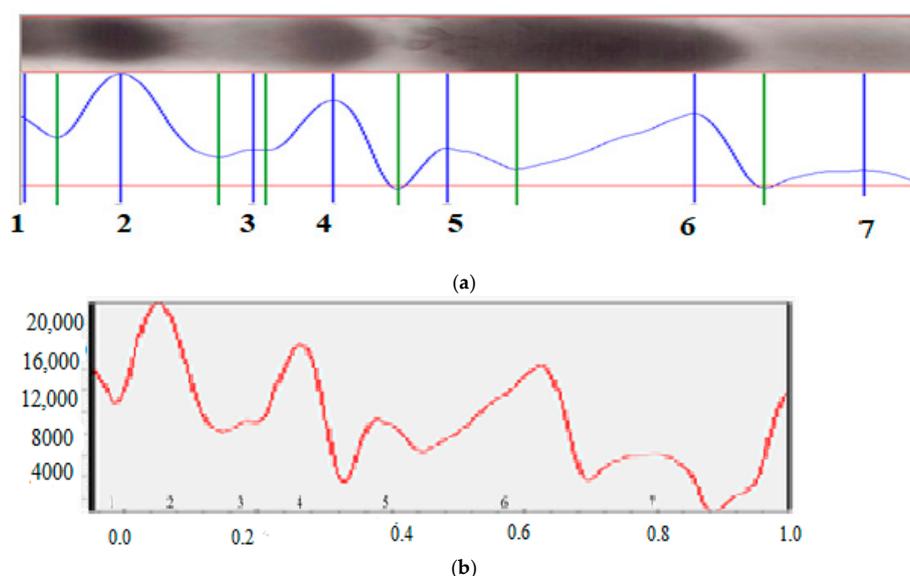


Figure 5. Chromatograms: (a) chromatographic plate view with eluent distribution, (b) chromatogram of lipid classes of *C. Sorokiniana* microalgae biomass

Fatty acids were studied by gas chromatography. This analysis showed that the composition of lipids is 80.02% unsaturated fatty acids (C18:1, C18:2, C18:3) and 19.98% saturated acids with the number of carbon atoms in the chain from 16 to 20 (Figure 6, Table 2). Among unsaturated fatty acids, α -linolenic acid was detected in the amount of 44.01% (Table 1) of the lipid, which belongs to the family of polyunsaturated (Omega-3) fatty acids. It regulates fat metabolism and vital activity of beneficial bacteria that live in the human intestines. It improves vision, relieves inflammation in the joints, improves brain function, provides immune system reinforcement, and helps to treat skin diseases, eczema, allergies and Alzheimer's disease. It should be noted that Omega-3 acids are not synthesized in the human body and enter it exclusively with certain foods (fatty fish, vegetable oils). In this regard, the solution to the issue of technological production of Omega-3 from *C. sorokiniana* microalgae seems to be quite reasonable from the standpoints of economy and affordability. Therefore, it is recommended to fractionate the obtained extract into unsaturated fatty acids that are part of Omega-3, and use the remaining fraction as biodiesel [60–62].

Table 2. Fatty acid composition of lipids derived from *C. sorokiniana* biomass.

N ₀	Component	Percentage, wt %
1	C16 Palmitic	14.74
2	C16:1 Palmitoleic	1.37
3	C17 Heptadecanoic	2.69
4	C 17:1 Heptadecenoic	0.45
5	C 18:1 n9 cis Oleinic	18.90
6	C18-2- n6 trans γ -Linolenic	2.90
7	C18-2 n6-cis Linolenic	7.34
8	C18:3 n6 Linolenic	6.88
9	C18:3 n3 α -Linolenic	44.01
10	C20:3 Eicosatrienoic	0.41
11	C22 Behenic	0.31
13	Total	100.00

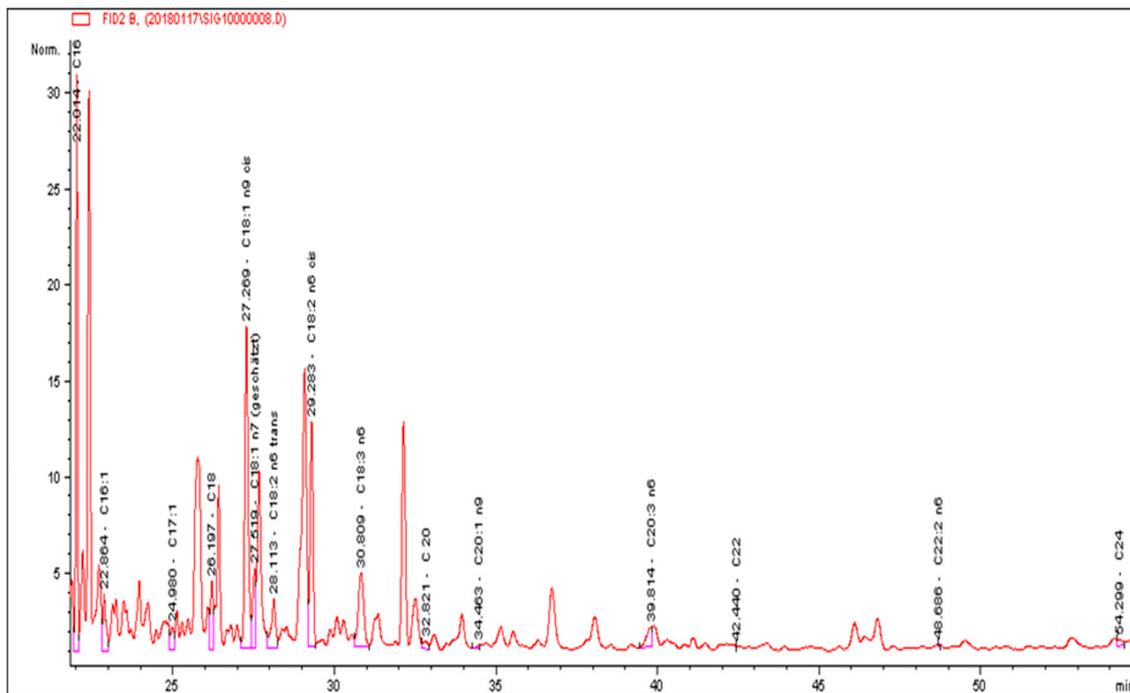


Figure 6. Chromatogram of total lipids obtained from *C. sorokiniana* microalgae biomass.

The resulting waste (residual biomass) after extraction is a light-gray powder (Figure 7, sorbent 1), consisting mainly of lignin and cellulose. To increase the sorption capacity, the residual biomass was subjected to heat treatment [56] (Figure 7, sorbent 2). The microstructural analysis showed the presence of a mesoporous surface from 0.5 to 2 microns and tubular pores (Figure 8).

It is technically difficult to use powdered thermally-treated residual biomass for wastewater treatment, because small particles are carried away with water. To increase the mechanical strength and usability, granular sorption materials were fabricated (Figure 8, sorbent 3).



Figure 7. External view of: 1—residual biomass of microalgae *C. sorokiniana*; 2—thermally-treated residual biomass of microalgae *C. sorokiniana*; 3—granular thermally-treated residual biomass of microalgae *C. sorokiniana* with chitosan.

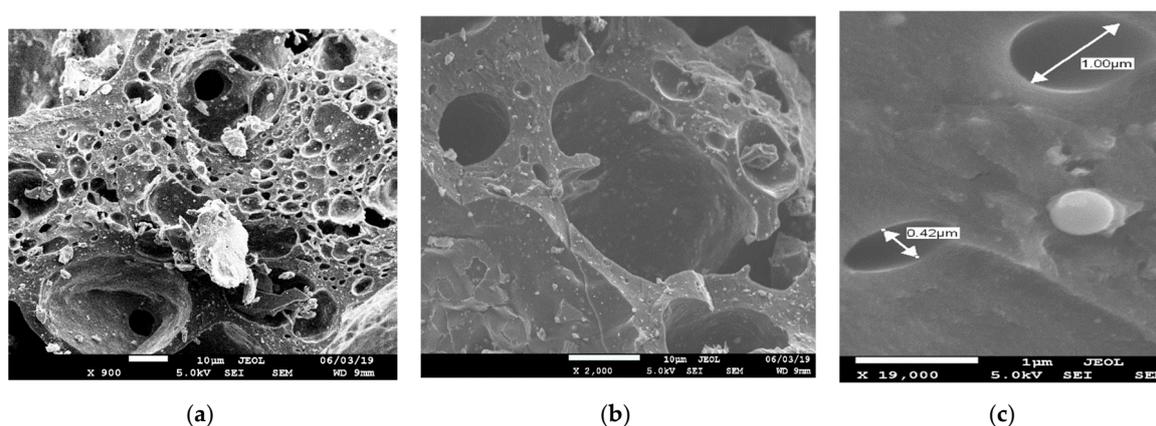


Figure 8. Surface morphology of the thermally-treated residual biomass of *C. sorokiniana* microalgae. expansion: (a) x 900, (b) x 2,000, (c) x 19,000

The obtained materials were examined for the ability to sorb PTE and REM from model wastewater. The maximum sorption capacity for PTE ($Zn + 2$, $Cd + 2$, $Cu + 2$) was calculated. Using the BET method, the specific surface of sorption materials and pore volume were calculated, Table 3.

Table 3. The maximum sorption capacity for sorbents made of residual biomass of *C. sorokiniana* microalgae and chitosan.

Sorbent	Sorption Capacity, A, mg/g				Specific Surface m^2/g	Pore Volume, cm^3/g	Average Pore Size, nm	Attrition, % Not More Than 0.5%
	Zn^{2+}	Cd^{2+}	Cu^{2+}	Total A, mg/g				
1	102.5	62.7	51.2	216.4	75.5	0.012	4–6	-
2	132.6	68.3	54.5	255.4	28.7	0.098	5–20	-
3	177.3	73.9	98.5	349.7	5.2	0.014	2–8	0.3

Table 3 shows that the total sorption capacity increases and reaches 349 mg/g when the residual biomass is thermally-treated and chitosan is added for granulation. Extraction of metal ions by residual biomass occurs due to chemisorption processes. When using thermally-treated residual biomass, it occurs due to adsorption processes (physical sorption) into the pores of the adsorbent. In case of granulated materials, the metal extraction occurs due to two sorption processes, namely chemisorption (due to the participation of functional groups of the chitosan structure) and adsorption (due to the porous surface). The sorption capacity of pure chitosan ranges between 95–225 mg/g [57,58]. The granulated sorbent from thermally-treated residual biomass and chitosan (sorbent No. 3) has the maximum sorption capacity and mechanical strength. Therefore, the sorption properties of sorbent No. 3 with respect to rare-earth metal ions were further investigated. Sorption isotherms were constructed for each metal separately. All isotherms are of the first type according to the Smith and Langmuir classification (Figure 9). The maximum adsorption capacities and Langmuir and Freundlich coefficients were calculated from isotherms (Table 4).

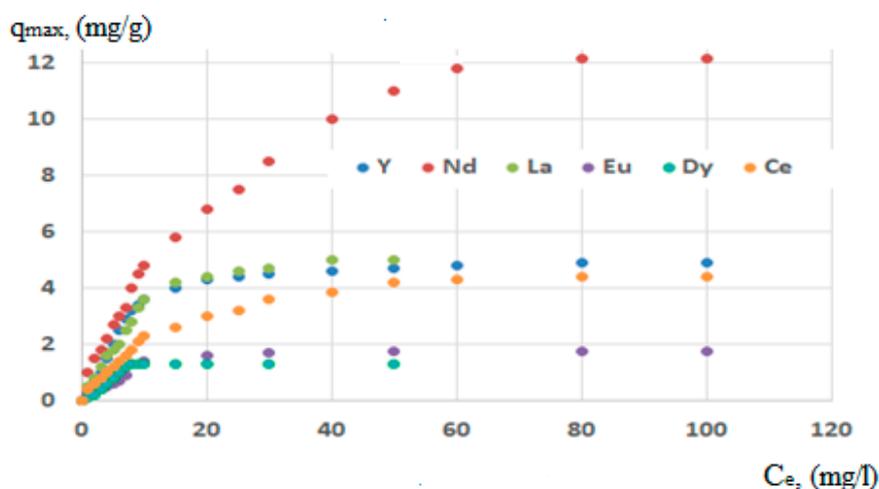


Figure 9. Isotherm of rare-earth metals (REM) adsorption from model solutions at pH = 4, sorbent No. 3.

Table 4. Maximum sorption capacity, coefficients of Langmuir and Freundlich adsorption isotherms for rare-earth metals by sorbent No. 3, at pH = 4.

Elements	Langmuir		Freundlich		
	q_{\max} (mg/g)	R^2	1/n	K_F	R^2
Ce (Cerium)	4.41	0.996	0.22	1.76	0.939
Dy (Dysprosium)	1.33	0.996	0.35	0.72	0.840
Eu (Europium)	1.74	0.991	0.33	0.94	0.920
La (Lanthanum)	5.02	0.999	0.31	2.03	0.928
Y (Yttrium)	4.85	0.999	0.30	1.74	0.880
Nd (Neodymium)	12.18	0.997	0.27	3.41	0.875
Calculated $\sum q_{\max}$ (mg/g)			31.9		

From Table 3 we can see that the correlation coefficients R^2 for both models of the isotherm are quite high. The Langmuir adsorption model is very well suited for calculating the maximum adsorption capacity. The $1/n$ values, which indicate the strength of adsorption, were 0.4, 0.44, and 0.48, therefore, the sorption process is advantageous. The values of $1/n$ between 0.1 and 1 imply successful adsorption [63]. The maximum total sorption capacity was 31.9 mg/g.

After extraction of PTE and REM ions, the problem of disposal of spent sorbents arises. For the disposal of spent sorbents, we suggest using them as additional fuel for combustion systems, as an additive to fossil fuels, etc. The calorimetric method was used to determine the higher heating value of spent sorbents, which amounted to $20.7 \text{ MJ} \cdot \text{kg}^{-1}$. When comparing this value with classical energy carriers (Figure 10), it was shown that sorbents from residual biomass have properties that are just as good as those of the classical fuel types (stone and brown coal). As a result of the analysis, it is possible to recommend using spent sorbents as additional fuel [64].

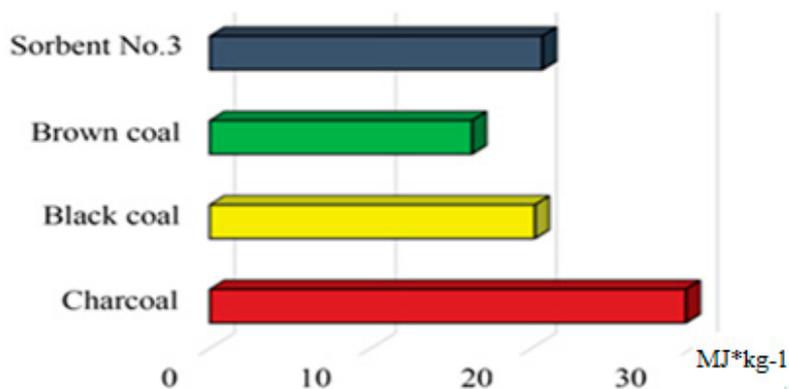


Figure 10. Specific combustion heat depending on the fuel type.

After combustion, ash contains heavy and rare-earth elements that, when separated, can be used economically, thereby solving the problem of biomining and closed-cycle zero-waste production, as shown in Figure 11.

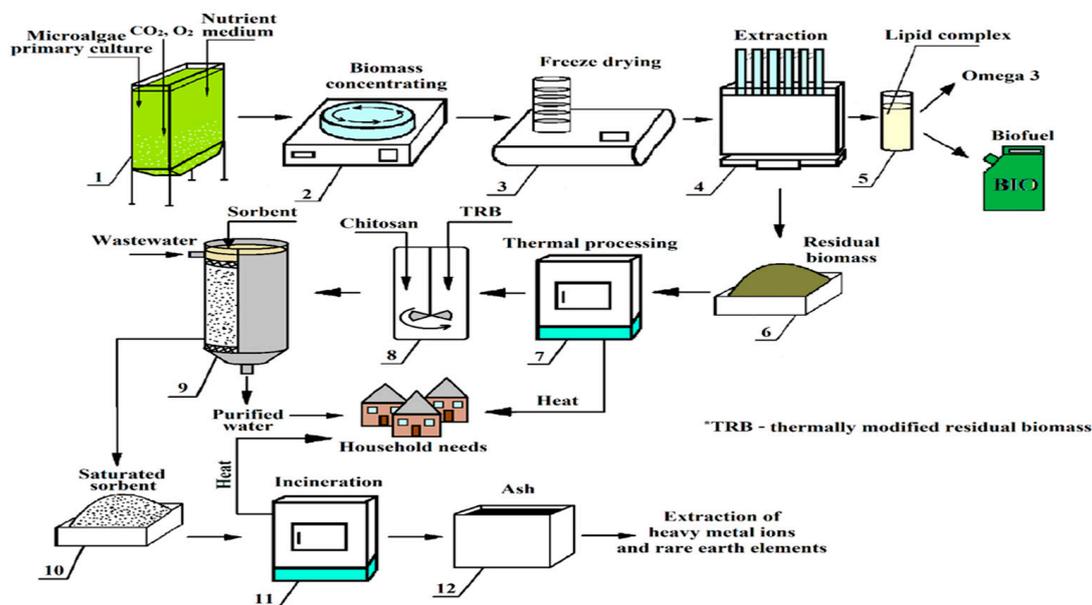


Figure 11. Closed cycle of microalgae biomass utilization with obtained products: 1—photobioreactor; 2—centrifuge; 3—extractor; 4—lipid tank; 5—lipid tank; 6—residual biomass tank; 7—oven for thermal processing of residual biomass; 8—granulator for sorbent obtaining; 9—adsorber for water purification; 10—spent sorbent; 11—oven for incineration of spent waste; 12—ash tank.

This scheme of microalgae biomass multifunctional use allows for obtaining a variety of Omega-3 materials for food purposes, biofuels and sorbents for environmental purposes and finally, heat for industry or residential heat-grids, or production of combined heat and power.

4. Conclusions

As a result of the work done, it was proven that microalgae biomass can be used to produce lipids and sorbents. The maximum yield of lipids from biomass was 20%. They contain unsaturated fatty acids, so we recommend using them for production of Omega-3, and the remaining lipid fractions for biofuels production.

The sorption properties of residual biomass were studied and a thermal modification was proposed that increases the total sorption capacity ($Zn + 2$, $Cd + 2$, $Cu + 2$) from 216.4 mg/g to 255.4 mg/g.

Using chitosan as a binder of granular heat-treated residual biomass contributed to an increase in the total metal ions absorption capacity ($Zn + 2, Cd + 2, Cu + 2$) up to 349.7 mg/g. We have proved that granular sorbents can recover rare-earth metals with a common sorption capacity of 31 mg/g. This allows us to recommend developed materials for water purification from PTE and REM.

The spent sorbents have a specific heat of combustion of $20.674 \text{ MJ} \cdot \text{g}^{-1}$, which is not worse than that of some classical types of fuel. Therefore, we recommend using them as fuel.

The proposed technologies for the cascade processing of microalgae biomass make it possible to obtain several useful products (lipids, sorbents, fuel) without waste generation, which corresponds to the global environmental concept.

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