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REMOVAL OF H_2S AND CO_2 FROM BIOGAS BY ALGAE-ASSISTED BIOELECTROCHEMICAL SYSTEM WITH OXYGENIC AND ANOXYGENIC PHOTOSYNTHESIS

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ABSTRACT

A bioelectrochemical system (BES) combining oxygenic and anoxygenic photosynthesis was investigated. The possibility of improving the composition of biogas by removing H_2S and carbon dioxide in the anode zone of the bioelectrochemical system and obtaining additional energy has been established. The dynamics of HS^- removal from model solutions in the BES anolyte at 3 operating modes were observed. Complete removal of sulfides in the anodic zone and the anaerobic photobioreactor was found in the BES operating option as a microbial fuel cell. At the same time, an increase in the concentration of sulfates was observed to varying degrees for the studied variants. The most probable mechanisms for the removal of H_2S in this combined system are the oxidation of sulfides by sulfur photoautotrophic bacteria present in the mixed consortium to sulfates and the bioelectrochemical oxidation of hydrogen sulfide on the surface of the anode to elemental sulfur and its other forms. The obtained results with real biogas passed through the BES anolyte and the anaerobic photobioreactor (APBR) are also positive. A complete purification of the biogas from H_2S and a significant removal of CO_2 (81 % - 85 %) were achieved, where the CH_4 content in the biogas reached 94.1 % - 96.2 %.

Keywords: bioelectrochemical systems, biogas, H_2S and CO_2 removal, anoxygenic and oxygenic photosynthesis, microalgae.

INTRODUCTION

Sulfates are easily transformed into toxic sulfide by sulfate-reducing bacteria (SRB) via the dissimilatory sulfate reduction pathway under anaerobic conditions and negatively impact the anaerobic digestion (AD) process. In anaerobic fermenters, sulfur exists in soluble (S^{2-}, HS^- and H_2S_{aq}) and gaseous (H_2S) forms depending on the environmental factors such as pH and temperature [1]. HS^- and H_2S_{aq} are usually the dominant sulfide species in the anaerobic fermenters, most of which operate at neutral pH and mesophilic temperature. However, a significant amount of sulfide is released in gaseous (H_2S) form in the produced biogas. The H_2S content of biogas typically varies from 0.1 % to 2 % (v/v), depending on substrate composition [2]. *Ex-situ* treatment methods have proven effective in removing H_2S from biogas and are widely used for full-scale applications. However, they require complex installations and operating costs due to the need for sequential multi-step processes [3]. *In-situ* methods remove or suppress sulfide formation during AD in digesters, and they do not require large separate sulfide removal facilities. Thus, they are technically simpler and more economical than *ex-situ* methods. In addition, *in situ* methods may prevent disruption of methanogenic activity due to the competition with SRB or direct sulfide toxicity [4].

The use of microalgae for biogas treatment to remove H_2S and CO_2 is from the last 10 - 15 years [5] and it falls under the so-called "biological methods" for treating biogas to improve its composition [2]. The application of an oxygenic process of photosynthesis

with microalgae for biogas treatment is difficult, due to the need for oxygen in the system and the danger of mixing the gas phase of biogas with the air used in oxygenic photosynthesis. However, sorption with CO_2 uptake by oxygenic microalgae has been demonstrated in several studies, both at laboratory and pilot scale [6], using an absorption column in which CO_2 is removed.

Unlike oxygenic photosynthesis, anoxygenic photosynthesis is much more suitable for the removal of H_2S from biogas because it takes place in one step and the risk of oxygen contamination in the gas phase is eliminated. Anaerobic H_2S removal processes use green sulfur bacteria (GSB) [2, 7] and/or a mixed culture of purple phototrophic bacteria (PPB) consisting mainly of purple sulfur bacteria (PSB) [8], which can oxidize sulfide to sulfate [9]. PPBs possess a photoautotrophic metabolism, using sulfides as an electron donor for inorganic carbon reduction and also for their growth and development [10]. This makes PPBs suitable in an H_2S removal process with simultaneous stoichiometric CO_2 removal at a ratio of 0.5 S/C (theoretical molar ratio) [7]. Another advantage of the process mediated by PPB is the reduced electrical energy required to form the infrared spectrum (optimal for the development of PPB), which is much less compared to the energy required to form the visible spectrum of light in other phototrophic processes. In addition, anoxygenic photosynthesis does not generate oxygen in the medium, as the case with oxygenic photosynthesis.

Bioelectrochemical systems (BESs) integrated into the anaerobic digestion process (through hybrid AD-BES systems) have attracted considerable interest in recent years, mainly with the possibility of bioelectromethanation, which increases methane, in the composition of biogas. It is more fully utilized the organic substrate and stabilization of the process is achieved [11]. Another important application of BES is related to the possibility of using H_2S accumulated in the environment, in the process of biomethanation with the parallel microbial sulfate reduction in the anode zone of BES, as a mediator in electronic transfer, and the generation of electricity in the system is carried out during the oxidation of the produced hydrogen sulfide on the surface of the anode (to elemental sulfur and other forms of it), whereby it is removed from the liquid phase [12].

The aim of this research is to establish the possibility of removing H_2S and CO_2 from the composition of biogas and obtaining additional energy by using a BES in which the processes of oxygenic and anoxygenic photosynthesis are combined, in the cathode and anodic zones, respectively. The removal of H_2S and CO_2 is expected to be realized through different mechanisms (absorption, uptake by the microbial consortium during photosynthesis and/or bioelectrochemical oxidation in the anode zone), through the biogas leaks in the anoxic photobioreactor volume and the anode zone of the BES. Establishing the mechanisms of H_2S and CO_2 removal in this combined system will be the basis for future practical application.

EXPERIMENTAL

Substrates, inoculum and enrichment of microbial communities

For the process of oxygen photosynthesis, a mixed culture of microalgae dominated by *Chlorella sp.* was isolated from natural waters. For the cultivation of the microalgae, the modified nutrient medium BG11 was used with the following composition for 1 L - 1.5 g $NaNO_3$, 0.5 g Na_2CO_3, 0.04 g K_2HPO_4, 0,075 g $MgSO_4.7H_2O$, 0.036 g $CaCl_2.2H_2O$, 0.045 g citric acid, 0.0015 g $(NH_4)_5[Fe(C_6H_4O_7)_2]$, 0.045 g EDTA (disodium salt), and 1 mL micronutrient solution consisting of 2.86 g L^{-1} H_3BO_3, 1.81 g L^{-1} $MnCl_2.4H_2O$, 0.222 g L^{-1} $ZnSO_4.7H_2O$, 0.39 g L^{-1} $NaMoO_4.2H_2O$, 0.079 g L^{-1} $CuSO_4.5H_2O$, 0.0494 g L^{-1} $Co(NO_3)_2.6H_2O$. The number of microalgae inoculum was approximately 10 % of the 3.0 dm^3 working volume of the aerobic photobioreactor together with the cathode zone of the BES (Fig. 1). Cultivation of the microalgae was carried out at room temperature in the range of 23ºC - 25ºC. The photobioreactor (PBR) was aerated by an air pump with a flow rate of 2.5 L h^{-1}, without further addition of CO_2 to the air.

For the process of anoxygenic photosynthesis, a mixed culture of anoxygenic phototrophic bacteria was used, isolated from a previously prepared Vinogradsky glass column [13] and inoculated with sediment microflora, cultivated at room temperature (21ºC - 24ºC) for a period of 60 days exposed to natural sunlight. The mixed culture, dominated by anoxic photoautotrophs, was then grown on a modified Ormerod medium [14], with added sources of carbon, nitrogen, and phosphorus, as well as $Na_2S.9H_2O$ according to Egger et al. [9]. The same nutrient medium was used in the experiments in the anoxic photobioreactor and as an anolyte in the BES (Fig. 1).

Description of the laboratory installation

A scheme of the laboratory installation of an integrated bioelectrochemical system and two photobioreactors is shown in Fig. 1.

The laboratory installation includes two photobioreactors - a photobioreactor for anoxic photosynthesis (3) and a photobioreactor for oxygenic photosynthesis (10). The photobioreactor for anoxic photosynthesis (3) with a working volume of the liquid phase of 0.8 dm^3 is a double hermetically sealed glass vessel of the "tube-in-tube" type. An IR-LED light source with a wavelength in the range 670 nm - 830 nm, with a spectrum maximum at 750 nm, illumination intensity 2600 - 3500 Lx and lighting mode 12 h light : 12 h dark is installed in the inner tube of the reactor. The liquid phase of the photobioreactor is continuously recirculated at a flow rate of 6 dm^3 h^{-1} by a peristaltic pump (6) through the anode zone of the BES.

The oxygen photobioreactor (10) is a plexiglass tube with an internal diameter of 85 mm, a height of 630 mm and a working volume of 2.5 dm^3. For effective photosynthesis, a plexiglass tube with an internal diameter of 36 mm is placed along the length of the photobioreactor, in which a fluorescent lamp type "SunGlo" with a power of 20 W in the lighting mode 12 hours of light : 12 hours of darkness is installed. From the bottom of the photobioreactor (PBR), the possibility of aeration with air is ensured by an air pump with a flow rate of 2 dm^3 in the 60 s. The liquid phase of the photobioreactor is continuously recirculated at a flow rate of 6 dm^3 h^{-1} by a peristaltic pump (6) through the cathode zone of the BES.

The bioelectrochemical system used is a classical H-shaped design, with equal volumes of the anode and cathode chambers of 0.5 dm^3. Graphite rods with a diameter of 8 mm and a length of 100 mm were used for the electrodes. A cation exchange membrane (CEM), CMI-7000S (Membrane International Inc.) with a diameter of 30 mm was used as the separator. In the preliminary studies conducted on BES operation in the microbial fuel cell (MFC) mode below, it was found that the optimum values of current density and power are obtained at an external load resistance in the range of 300 Ω - 400 Ω. In the BES mode as a microbial electrolysis cell (MEC), an additional external DC voltage of 0.6 V was supplied from a stabilized rectifier model- PSP-405. For the treatment of biogas in the anoxic photobioreactor and the anode zone of the BES, the possibility of dosing biogas containing H_2S and CO_2 is foreseen. For this purpose, according to the technological scheme (Fig. 1),

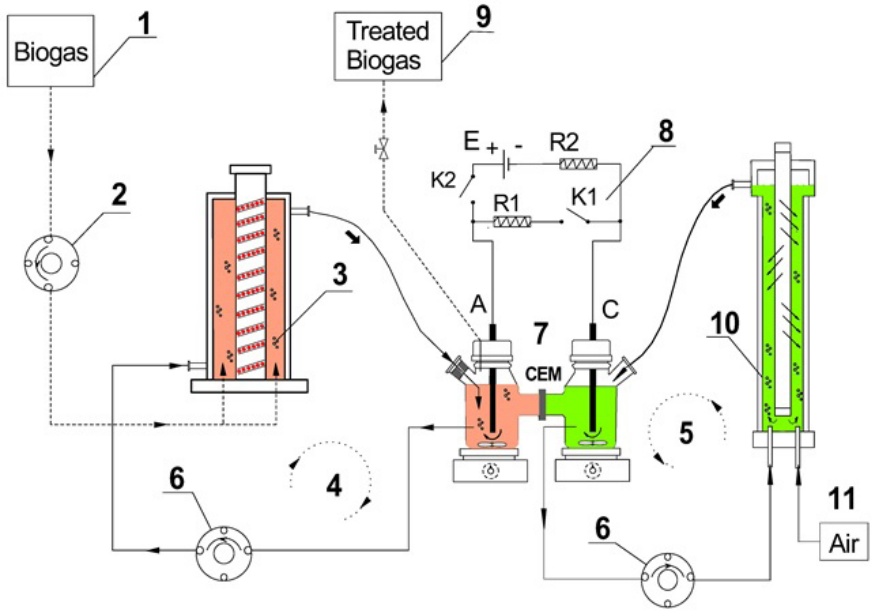

Fig. 1. Technological scheme of the laboratory installation: 1 - tank for initial unpurified biogas, 2 - biogas dosing pump, 3 - anaerobic photobioreactor with IR-LED light source, 4 - recirculation loop of the BES anode zone, 5 - recirculation loop of the BES cathode zone, 6 - recirculation pumps, 7 - bioelectrochemical system (BES), 8 - load circuit of BES, 9 - tank for treated biogas, 10 - photobioreactor for cultivating oxygenic microalgae, 11 - air pump.

the unpurified biogas from the gas tank (1) by a peristaltic pump (2) is dosed through the volume of the anoxic photobioreactor, and then, together with the liquid phase, passes through the anode zone of the BES and finally enters the collector tank (9). The biogas tanks were gas balloons with a volume of 2 dm^3. The crude biogas was obtained according to parallel studies [15, 16] for the biomethanation of an ethanol stillage in a laboratory plant with the composition of the constituent gases indicated below.

Analytical methods

The volume of biogas was measured using a milli-gas counter model "Ritter MGC-1", and the content of CO_2, CH_4, O_2, H_2S and H_2 in biogas was determined using a portable gas analyzer "Draeger X-am 7000". At various points in the laboratory installation the possibility of continuous (online) measurement of dissolved oxygen, pH, voltage, electrical conductivity, temperature and illuminance is provided, using Vernier^R BTA sensors and visualization and recording of data through the LabQuest^R interface.

The pH, TDS and Eh parameters were measured at certain points of the laboratory installation. Conductivity, pH and ORP were measured using a WTW Multi 3510 IDS and corresponding electrodes. The concentration of sulfates was determined spectrophotometrically at λ 420 nm, using $BaCl_2$ reagent. The concentration of hydrogen sulfide in the liquid phase was measured using Nanocolor test 1-88/05.09 at λ 620 nm. A Bürker light microscope counting chamber (BoecoR, BM-800) was used to determine the number of microalgae, as well as a parallel determination of the optical density of the cell suspension during the cultivation of the microalgae at a wavelength of 650 nm and a red filter.

Working with bioelectrochemical system and electrochemical analyses

In the periodic mode of operation of the two photobioreactors, three different variants of BES operation were investigated, with the aim of removing unwanted components from the biogas composition. According to previous studies, a generation time of 20 days was observed, by establishing the growth curve of the used microbial consortium dominated by *Chlorella sp.* used in oxygenic photosynthesis [16]. During the conducted research, both photobioreactors (together with their adjacent volumes in the cathode and anode zones) were filled with the above-described nutrient media, inoculated and cultivated at room temperature with the corresponding phototrophic microorganisms. To ensure approximately the same conditions, in the period between 10th and 20th day of the cultivation cycle (the exponential growth phase of the mixed microbial consortia), experiments were conducted with the inclusion of BES to both photobioreactors. Each of the experiments performed was done after replacing the nutrient medium in the photobioreactors and starting a new cultivation cycle, always between 10^{th} and 20^{th} day from the beginning of the process.

Three operating modes of the bioelectrochemical system (BES) were investigated. The first mode is without the participation of the BES, with an open circuit of the BES (no load between the anode and the cathode). In the second mode the BES is operating as a microbial fuel cell (MFC), where a load of 300 Ω is applied, the third mode of the BES is as a microbial electrolysis cell (MEC), with an external voltage of 0.6 V applied between the electrodes and a load resistance of 10 Ω.

The electrical parameters of the BES were measured with a Keithley 175 digital multimeter, and a precision potentiometer with a maximum value of 11 kΩ was used for the load resistance. The maximum power value P_{max}, was established by constructing polarization curves. The current and power density is calculated based on the geometric area of the electrodes in the anode/cathode chambers and the voltage across the load resistors (R1/R2).

RESULTS AND DISCUSSION

To establish the possibilities of H_2S and CO_2 removal from the composition of biogas in the anode zone of BES, two groups of experiments were carried out. The first group of experiments was conducted with a model composition of the anolyte with an addition in the liquid phase of sulfides in the form of $Na_2S.9H_2O$, while controlling the change in the concentration of sulfates and sulfides over a period of 10 days. The second group of experiments was performed by passing real biogas containing H_2S and CO_2 through the anoxic photobioreactor and the anode zone, and monitoring the influence on the gas composition and the changes in H_2S and sulfates in the liquid phase concentrations.

Before the start of the experiments, the electro-

chemical characteristics of the BES in the microbial fuel cell (MFC) mode were investigated to establish the load resistance (R1- Fig. 1) at which optimal values of the current density and power of the fuel cell are reached. For this purpose, the polarization curves and the power curves were established (Fig. 2). The measurements were made during the exponential phase of the cultivation of the oxygenic microalgae, during the light cycle of photosynthesis.

The obtained results of the polarization curves show that the maximum values of current density and power are reached, respectively - 92.7 mA m^{-2} and 30.1 W m^{-2}, and these values were achieved at a load resistance of 300 Ω (Fig. 2).

In the first series of experiments, sulfides (in the form of $Na_2S.9H_2O$) were added to the nutrient medium (respectively to the anolyte) used for the cultivation of anoxygenic photoautotrophs until an HS^- concentration of 0.5 g L^{-1} was reached. Previously pH of the medium was adjusted to 7.50 with 0.1N NaOH solution. Under these conditions, three modes of the BES study were carried out - the first one was without the participation of the BES (with an open electric circuit of the BES), the second one was with the operation of the BES as a microbial fuel cell (MFC) with a load of 300 Ω and the third mode of the BES is like a microbial electrolysis cell (MEC), with 0.6 V applied external voltage and load resistance (R2) of 10 Ω. The obtained results of the dynamics of sulfates and dissolved sulfides (in the form of HS^-) in the anolyte are presents on Fig. 3.

The obtained results show that for all three modes, sulfides are removed from the BES anolyte to varying degrees. For example, without BES mode, 64 % sulfide removal is achieved in the anoxic photobioreactor in 9 days. On the other hand, the concentration of sulfates in the medium increased during this period from 365 mg L^{-1} to 559 mg L^{-1}, which is most likely due to the oxidation of sulfides by sulfur photoautotrophic bacteria present in the mixed consortium. The influence of BES on the removal of sulfides in the anolyte turns out to be very strong - when operating the system as a microbial fuel cell, sulfides are almost completely removed on the 9th day, with their concentration reaching 9.0 mg L^{-1}, at initial 480 mg L^{-1}, i.e. 98.1 % (Fig. 3). At the same time, when an additional external voltage of 0.6 V is applied in the mode as microbial electrolysis cell, even better results are obtained - in 5 days, almost complete removal of sulfides from the anolyte up to 99.5 % is achieved. Regarding sulfates, the results clearly show that their concentration decreases with the use of BES in MFC and MEC modes, this decrease being greater for MEC. This can be explained by the deposition of S^0 on the anode surface during the electrochemical oxidation of H_2S. An interesting result is also the slight increase in the sulfate concentration after the 6th day of MEC operation, this could be due to the secondary oxidation

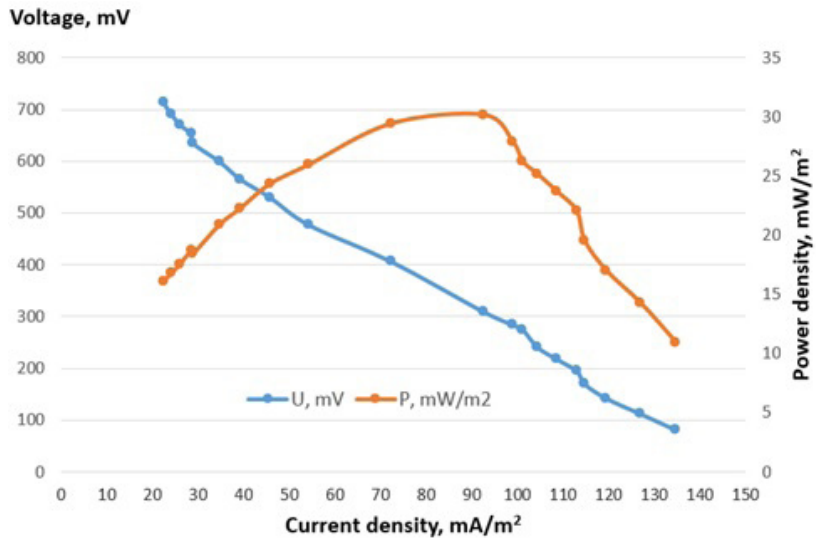

Fig. 2. Polarization curve and power curve of BES for MFC mode.

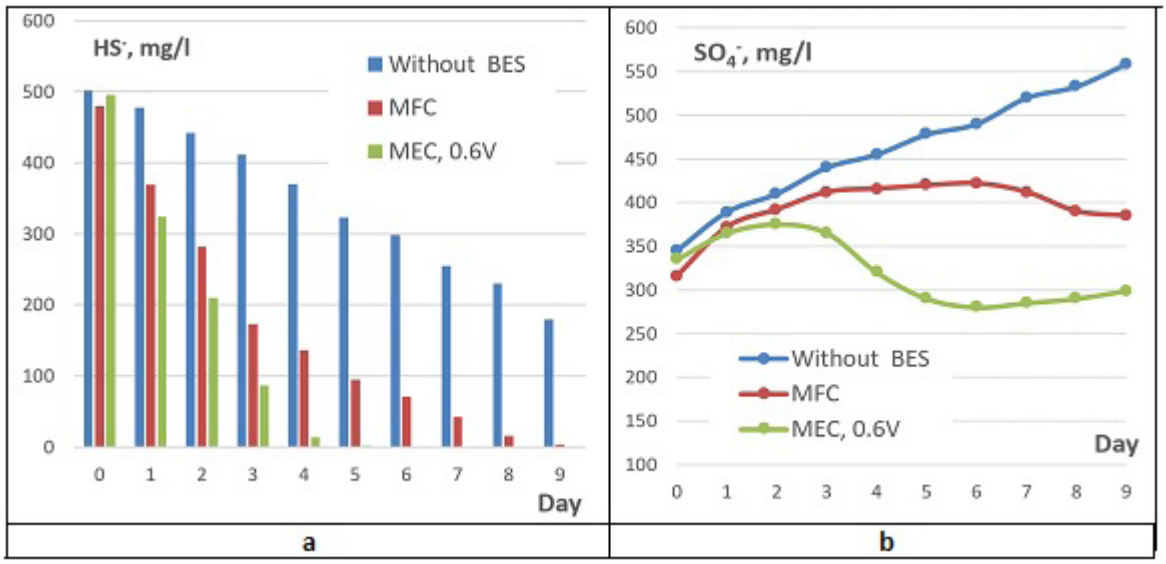

Fig. 3. The dynamics of HS^- (a) and sulfates (b) in the anolyte over a period of 10 days at three different BES operating modes.

Table 1. Change in the biogas composition used for treatment in the combined aerobic-anaerobic phototrophic BES system.

Gas composition	Initial biogas	Biogas after treatment in an anoxic photobioreactor (APBR)	Biogas after treatment in MFC-APBR	Biogas after treatment in MEC-APBR (0.6V)
CH_4, vol. %	59.1-64.5	91.6-94.3	92.5-95.5	94.1-96.2
CO_2, vol. %	31.4 -34.1	5.6-8.4	4.8-7.7	4.4-6.5
H_2S, vol. %	0.111- 0.085	0.054-0.033	0.015-0.005	0
H_2, vol. %	0.9- 1.0	0.45-0.21	0	0

of elemental sulfur deposited on the anode by sulfur-oxidizing bacteria (SOB), which are probably present in the microbial consortium. An analogous mechanism of secondary oxidation of sulfur to sulfates on the anode surface in MFC was also described by Blázquez et al. [17].

In the second group of experiments, really produced biogas during the biomethanation process of waste ethanol stillage was passed through the volume of the anoxic photobioreactor and the anodic zone of the BES. The composition of the initial biogas in percentages by volume is indicated in Table 1. The treated biogas was passed for 8 days, successively through the volume (Fig. 1) of an anoxic photobioreactor (APBR) and the anode zone of the BES with a flow rate of 250 ml for 24 h from a gas balloon (1) (volume 2 dm^3) with initial biogas and collected in a collector balloon (2) (volume 2 dm^3).

The obtained results show an effective removal of H_2S (up to 100 %) in the MEC-APBR mode, up to 86.5 % in the MFC-APBR mode and 51.3 % in biogas treatment only in an anoxic photobioreactor (APBR), respectively.

Regarding the CO_2 removal from the biogas composition, it can be seen (Table 1) that in all three modes the removal is comparable (from 81 % to 85 %). These results show that BES does not have a strong impact on the amount of CO_2 in the gas composition of the treated biogas, and the main impact is related to the photosynthesis process in APBR.

Fig. 4 shows photographs images of a culture suspension of microalgae dominated by *Chlorella sp.* (cathode zone) with typical cell sizes of 3 µm - 4 µm (Fig. 4(a)) and a light microscope image of a mixed culture of anoxygenic phototrophic microorganisms (anode zone) with sizes of cells 1-3 µm (Fig. 4(b)). An interesting task for future research is determining the exact species composition in the microbial consortia used.

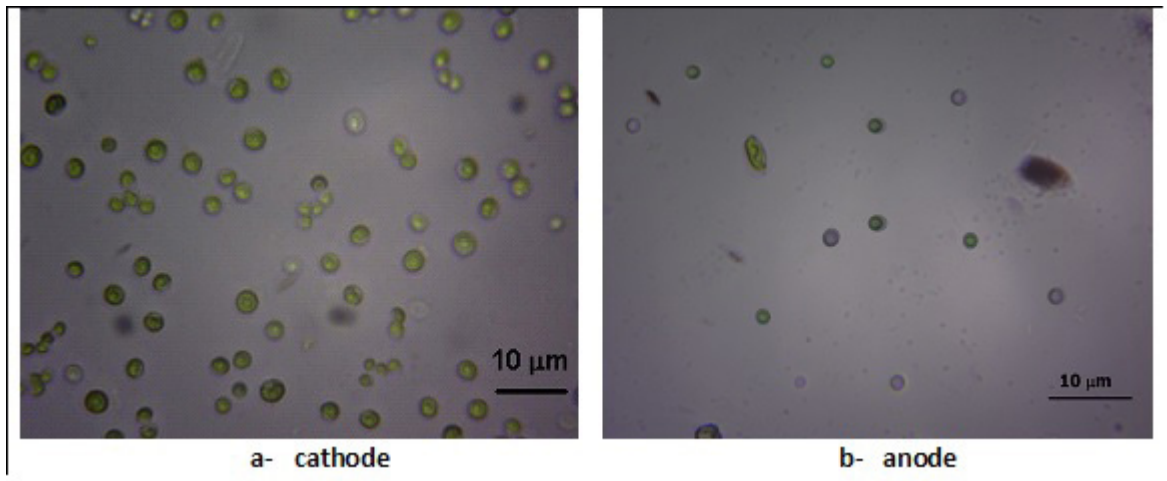

Fig. 4. Morphological characteristics and light microscope images of microalgae dominated by *Chlorella sp.* (cathode area) (a) and an image of a mixed culture of anoxygenic phototrophic microorganisms in the anode area of BES (b).

CONCLUSIONS

In the present study, the possibility of H_2S and carbon dioxide removing from the biogas composition and obtaining additional energy was demonstrated by using a bioelectrochemical system in which the processes of oxygenic and anoxygenic photosynthesis are combined, respectively, in the cathodic and anodic zones. The dynamics of sulfide removal from model solutions in the BES anolyte under three operating modes were observed. Complete removal of sulfides in the anode zone and the anaerobic photobioreactor was found in the BES mode as MFC. At the same time, an increase in the concentration of sulfates was observed to varying degrees for the studied variants. The probable mechanisms for H_2S removal in this combined system consists in the oxidation of sulfides by sulfur photoautotrophic bacteria present in the mixed consortium to sulfates and the bioelectrochemical oxidation of hydrogen sulfide on the anode surface to elemental sulfur and its other forms. The obtained results with real biogas passed through the BES anolyte and the anaerobic photobioreactor (APBR) are also positive. A complete purification of the biogas from H_2S and a significant removal of CO_2 (81 % - 85 %) was achieved, where the CH_4 content in the biogas reached 94.1 % - 96.2 %.

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