ENVIRONMENTAL PROBLEMS

Vol. 7, No. 3, 2022

CLEANING OF GAS EMISSIONS BY BIOLOGICAL METHOD

Vasyl Dyachok, Liubov Venher, Serhiy Huhlych, Iryna Svjantko

Lviv Polytechnic National University,
12, S. Bandery Str., Lviv, 79013, Ukraine
ljuvenger77@gmail.com

https://doi.org/10.23939/ep2022.03.147

Received: 11.07.2022

Abstract The paper shows the possibility of using chlorophyll-synthesizing microalgae of Chlorella Vulgaris to purify biogas from carbon dioxide (CO_2), hydrogen sulfide (H_2S) and ammonia (NH_3). Experimental dependences of the dynamics of CO_2 uptake by microalgae under the action of H_2S inhibitor and NH_3 activator are presented. A mathematical description of the growth of biomass of microalgae Chlorella Vulgaris depending on the concentration of hydrogen sulfide and ammonia was obtained. The optimal values of hydrogen sulfide and ammonia concentration for the efficient process of carbon dioxide uptake by chlorophyll-synthesizing microalgae Chlorella Vulgaris from biomethanization gas have been established.

Keywords: microalgae Chlorella Vulgaris, biogas, carbon dioxide (CO_2), hydrogen sulfide (H_2S), ammonia (NH_3), nitrogen oxides (N_xO_y), sulfur dioxide (SO_2).

1. Introduction

The rapid development of industry has led to the depletion of world fossil fuel reserves. Therefore, renewable energy technologies have been actively introduced recently, in particular, the production of various biofuels, the most available of which today is biomethane gas – biogas. The main disadvantage of biogas is the significant number of impurities, in particular, CO_2, H_2S and NH_3. Biogas needs purification for two main reasons: to increase its calorific value and to reduce equipment damage and adverse effects on human health and the environment to the toxic effects of H_2S (Allegue, 2014).

Technologies for biogas purification have been developed and are available today. They include physical absorption and chemisorption, cryogenic and membrane separation. However, physicochemical treatment methods are not only expensive, as they require a lot of energy, materials and reagents, but also generate a significant volume of wastewater that pollutes the environment (Awe, 2017). In addition, polluting gases captured in this way are dangerous during storage, transportation etc. At the same time, there are also biological methods of purification, in particular, using micro-algae with photosynthetic activity, which eliminates these problems to some extent.

The biological treatment makes it possible to transform pollutants into harmless products of microorganisms and biomass. At present, microalgae deserve special attention. They are quite effective converters of solar energy with well-organized stages of reduction of CO_2 to a whole complex of biomolecules, including carbohydrates, proteins, and lipids, which can be involved in further biotechnological transformation into a variety of target products. Microalgae can grow quite quickly in more difficult conditions of their unicellular structure. The microalgae of Chlorella Vulgaris are considered to be one of the most productive. This genus of microalgae has long been known and well studied, which is an undoubted advantage for their use in industry. Along with high biomass productivity, these cells have several features that allow them to be considered the most suitable for biotechnological processes as a substrate. The advantage of microalgae of Chlorella Vulgaris is their exceptional adaptability to environmental changes. (Dyachok, 2017).

For citation: Dyachok V., Venher L., Huhlych S., Svjantko I. (2022). Cleaning of gas emissions by biological method. *Journal Environmental Problems*, *7*(3), 154–162. DOI: https://doi.org/10.23939/ep2022.03.147

Using microalgae to sorb carbon dioxide, which is generated during methane fermentation, will solve the problem of the purification of biogas from hydrogen sulfide and ammonia. As sulfur and nitrogen are trace elements necessary for the activity of microalgae, they can be consumed in specific concentrations without inhibiting their growth. Moreover, this method of using microalgae is interesting not only for the purification of biogas but also because it allows getting valuable biomass, which is used as raw material in various biotechnological processes.

Many works have been devoted to the study of the influence of carbon dioxide, sulfur dioxide, and nitrogen on the growth of microalgae, and this issue has been sufficiently covered in (Dyachok, 2020).

At present, information on the impact of associated gases – products of biomethanization, hydrogen sulfide H_2S and ammonia NH_3 on the growth and development of microalgae is extremely insufficient.

To achieve this aim, the following task was set: establishing the optimal concentrations of hydrogen sulfide H_2S and ammonia NH_3, at which the absorption of carbon dioxide CO_2 by microalgae of the genus Chlorella is the most effective.

2. Materials and Methods

The average chemical composition of biogas is known from the literature. Biogas consists of methane (CH_4: 50–75 vol. %), carbon dioxide (CO_2: 25–50 vol. %), water vapor (H_2O: 0–10 vol. % , nitrogen (0.01–5 Vol. %), oxygen (0.01–2 vol. %), hydrogen (H_2: 0–1 %), ammonia (0.01–2.5 mg/m³) and hydrogen sulfide (H_2S: 10-30,000 mg/ m³) (M. Kaltschmitt, 2016). Microalgae Chlorella Vulgaris was taken from natural conditions (Kaltschmitt, 2016). To study the growth and development of microalgae, we took values of concentrations of sulfide HS^- anion and ammonium NH_4^+ cation, which correspond to the values of volume pressures of these pollutants in biogas.

The growth dynamics of Chlorella Vulgaris microalgae was studied for the corresponding values of the concentration of HS^- anion sulfide by adding sodium sulfide Na_2S, and ammonium NH_4^+ cations introduced by the adding NH_4OH ammonia water. Sodium sulfide and ammonia water were applied once at the beginning of the experiment. Cultivation of microalgae was performed in photobioreactors for 14 days at a temperature of 30 ± 2 °C. In all cases, the pH was within rational values for the cultivation of Chlorella Vulgaris.

There were five samples in the experiment and control:

- Control – the environment for the cultivation of microalgae without HS^-;
- Sample 1 – microalgae with the content of HS^- at a concentration of 170 g/m^3, which corresponds to 0.5 vol. % of hydrogen sulfide in biogas;
- Sample 2 – microalgae with the content of HS^- at a concentration of 340 g /m^3, which corresponds to 1 vol. % of hydrogen sulfide in biogas;
- Sample 3 – microalgae with HS^- content – at a concentration of 510 g/m^3, which corresponds to 1.5 vol. % of hydrogen sulfide in biogas;
- Sample 4 – microalgae with HS^- content – at a concentration of 765 g/m^3, which corresponds to 2 vol. % of hydrogen sulfide in biogas;
- Sample 5 – microalgae with HS^- content – at a concentration of 1147 g/m^3, which corresponds to 2.5 vol. % of hydrogen sulfide in biogas.

The ammonia content in biogas can reach 1vol. %, depending on the raw material taken for methane fermentation according to the literature (Dyachok, 2021). Therefore, in the work, the cultivation medium contained:

- Sample 1 – NH_4^+ at a concentration of 228 g/m^3, corresponding to 0.25 vol. %;
- Sample 2 – NH_4^+ at a concentration of 455 g/m^3, corresponding to 0.5 vol. %;
- Sample 3 – NH_4^+ at a concentration of 910 g/m^3, corresponding to 1 vol. %;
- Sample 4 – NH_4^+ at a concentration of 1365 g/m^3, corresponding to 1.5 vol. %;
- Sample 5 – NH_4^+ at a concentration of 1820 g/m^3, corresponding to 2.0 vol. %, respectively;
- Control – without NH_4^+.

The increase in the biomass of microalgae under such conditions was determined by photocolorimetric method using a blue light filter according to the law of Bouguer-Lambert-Ber (Poltorak, 1972). The photocolorimetric method was implemented on a photocolorimeter AP-101 (manufactured in Japan). Since the optical density is proportional to the content of microalgae in the culture medium, the obtained experimental data on the accumulation of microalgae biomass depending on the time within the studied values of HS^- and NH_4^+ concentration correspond to the values of optical densities. The results of the study at the same initial content of microalgae cells 0.2 mg/ml in photobioreactors are presented in Fig. 1 and Fig. 2.

3. Results and Discussion

The growth of microalgae of Chlorella Vulgaris during 14 days at different contents of HS^- anion sulfide is illustrated in Fig.1. The graph in the figure shows that the first day can be considered a period of adaptation, after which the sample growth increases rapidly. This does not continue for all samples until the end of the experiment – 14 days. The control from the second day passes the phase of exponential growth and from the fourth curve of control goes to the plateau, to the stationary phase of growth.

The largest increase in biomass was observed in Sample 1 and then in Sample 2. Samples 3 and 4 are almost at the same level. Sample 5, after a slight increase in growth, decreases, and ultimately cell death is observed, accompanied by a downward movement of the curve.

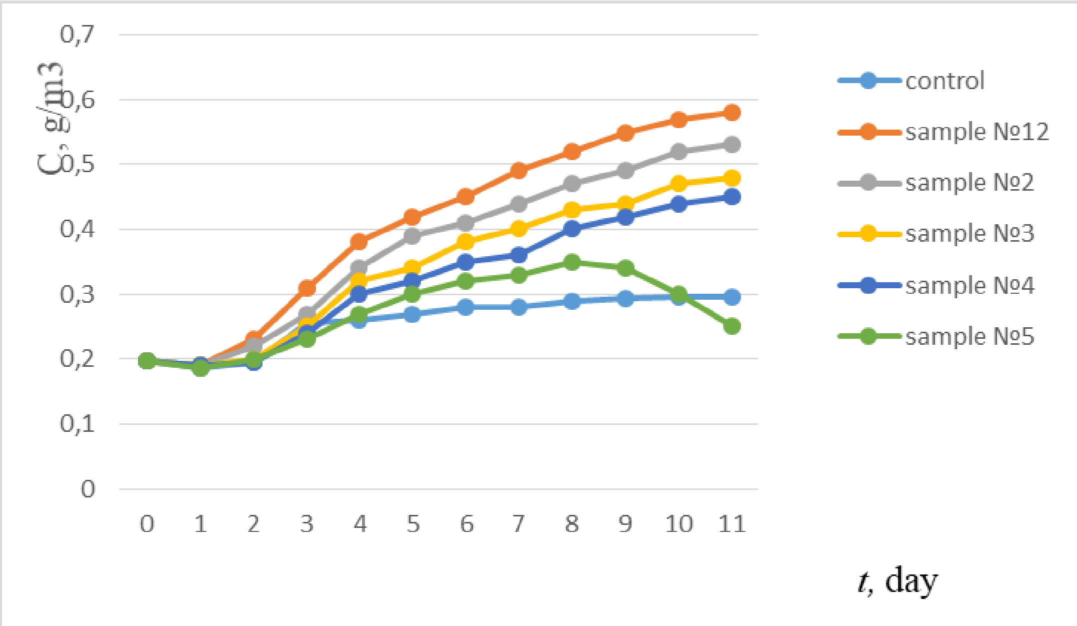

Fig. 1. The dependence of the change in the content of microalgae cells in the cultivation medium over time at appropriate concentrations of HS^-

Thus, the greatest increase in biomass is characteristic of cultures grown in a medium with a concentration of sulfide anion 390 g/m^3, which is twice as high as under control conditions. Higher values of the concentration of sulfide anion in the environment lead to a decrease in biomass growth, up to a negative – Sample 5. This is due to the fact that at the beginning of the study, Chlorella Vulgaris cells are not adapted, respectively, sulfide anion acts as a growth inhibitor, which cannot be said about the control microalgae. The control goes through a phase of adaptation, and cell growth reaches a plateau as the culture medium is depleted of sulfur that was in the nutrient medium. Accordingly, growth is reduced also due to the lack of this macronutrient. In samples with a higher value of sulfur in the form of sulfide anions, on the contrary, the content of the inhibiting substance, sulfides, decreases over time as they are oxidized to sulfites and sulfates, which are the main assimilative form for the microalgae of Chlorella Vulgaris.

The lower the concentration of sulfides, the faster most of them will turn into sulfites and sulfates. Therefore, the growth of cells in Sample 1 after adaptation quickly reaches the plateau, while Samples 2, 3 and 4 continue to divide more slowly. By the end of the experiment, the greatest relative cell growth was observed for Sample 1 because of the highest concentration of assimilable sulfur in the form of sulfites and sulfates, and sulfur is an essential and necessary element for normal cell division. In the same sample, the greatest increase in microalgae biomass is observed, which is probably a rational value of HS^- sulfide anion concentration for CO_2 absorption and increase in Chlorella Vulgaris biomass, and this concentration value does not adversely affect the development of microalgae.

Ammonia generated as a result of biomethanization can also be used as an energy material necessary for the activity of microalgae cells.

The required energy will be formed as a result of enzymatic reactions of oxidation of ammonia and ammonium salts and then nitric acids.

This assumption is confirmed by the obtained data presented in Fig. 2. The figure shows that the cations NH4+ contribute to the absorption of carbon dioxide, which is reflected in the growth of the microalgae biomass. The increase in the concentration of microalgae cells significantly depends on the concentration of NH_4^+ canions that act as activators of carbon dioxide absorption of CO_2. From the first to the fourth sample, we observe an increase in microalgae, which is much faster than in the control sample in which no other canions were added, only microalgae and nutrients.

We should also pay attention to Sample 5, which in comparison with others, after a slight increase, goes to the plateau and then begins to decline, indicating a detrimental concentration of NH_4^+ cations for the growth and development of microalgae.

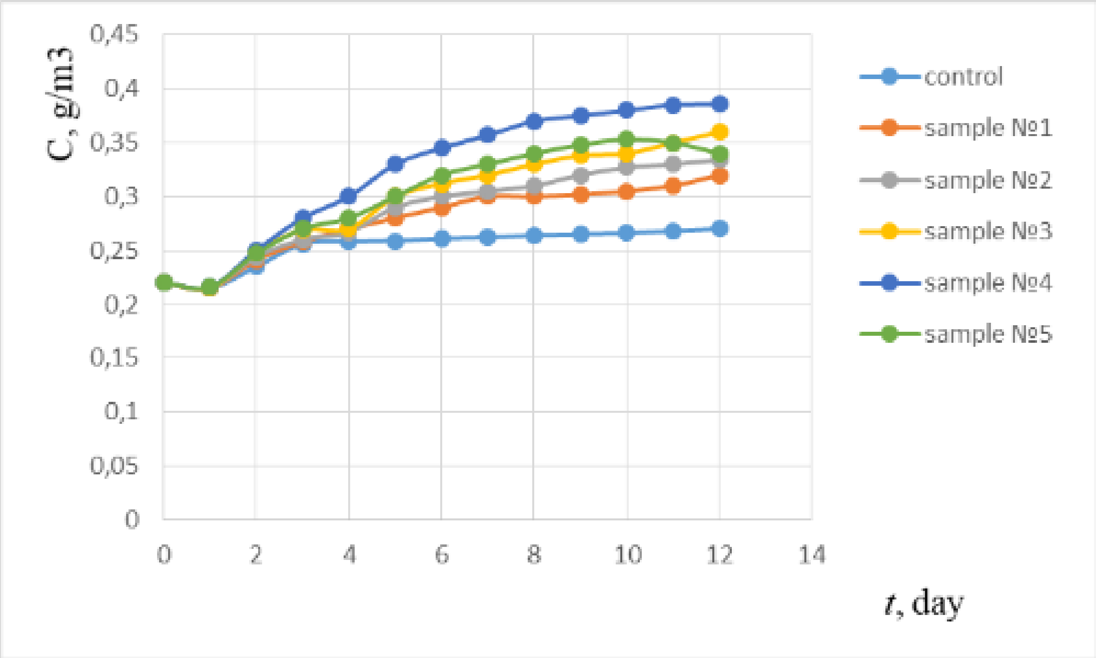

Fig. 2. The dependence of the change in the content of microalgae over time at appropriate concentrations of NH_4^+

Therefore, according to experimental studies, the most favourable for the growth and development of microalgae Chlorella Vulgaris and the absorption of carbon dioxide are the values of ion concentrations: HS^- – 0.17 g/m^3 and NH_4^+ – 910 g/m^3, which corresponds to 0.5 vol. % of hydrogen sulfide and 1.0 vol. % of ammonia in biogas.

It is logical to assume that the synergy effect will occur under the found optimal values of NH_4^+ and HS^- ion concentrations This assumption was confirmed by the experiment. The following values of concentrations were loaded into the photobioreactor under conditions similar to those previously described:

- Sample 1 – HS^- at a concentration of 170 g/m^3 and NH_4^+ – 1365 g/m^3, corresponding to 0.5 vol. % of hydrogen sulfide and 1.5 vol. % of ammonia in biogas;
- Sample 2 – HS^- at a concentration of 170 g/m^3 and NH_4^+ 1365 g/m^3, which corresponds to 0,5 vol. % of hydrogen sulfide and 1,0 vol. % of ammonia in biogas;
- Sample 3 – HS^- at a concentration of 340 g/m^3 and NH_4^+ – 1820 g/m^3, which corresponds to 1.0 vol. % of hydrogen sulfide and 1.5 vol. % of ammonia in biogas;
- Sample 4 – HS^- at a concentration of 340 g/m^3 and NH_4^+ – 1620 g/m^3, corresponding to 1.0 vol. % of hdrogen sulfide and 1.5 vol. % of ammonia in biogas;
- Sample 5 – HS^- at a concentration of 1147 g/m^3 and NH_4^+ – 1820 g/m^3, corresponding to 2.5 vol. % of hydrogen sulfide and 2.0 vol. % of ammonia in biogas.

The results of this experiment are presented in Fig. 3.

Based on the data of experimental studies and mathematical processing of the obtained results, we can see that the maximum increase of chlorophyll-synthesizing microalgae Chlorella is achieved by the ratio of NH_4^+; and HS^- ion concentrations; which were added to the first sample, namely 1.5 vol. % of ammonia and 0.5 vol. % of hydrogen sulfide in biogas. Fig. 5 also shows that Sample 2 has a rapid increase compared to others. Sample 2 contains 1.0 vol. % of ammonia and 0.5 vol. % of hydrogen sulfide in biogas. Moreover, the increase in microalgae in both samples far exceeds the increase in the individual action of hydrogen sulfide and ammonia in biogas, see Fig. 1 and 2. At concentrations of 1 vol. % of hydrogen sulfide and the two most optimal values of ammonia concentrations of 1 vol. % and 2 vol. %, an increase is also observed, although lower than in previous studies, 0.5 vol. % of hydrogen sulfide and 1 vol. % and 2 vol. % of ammonia in biogas.

At concentrations of 2.5 vol. % of hydrogen sulfide and 2 vol. % of ammonia, the death of the microalgae Chlorella Vulgaris is observed.

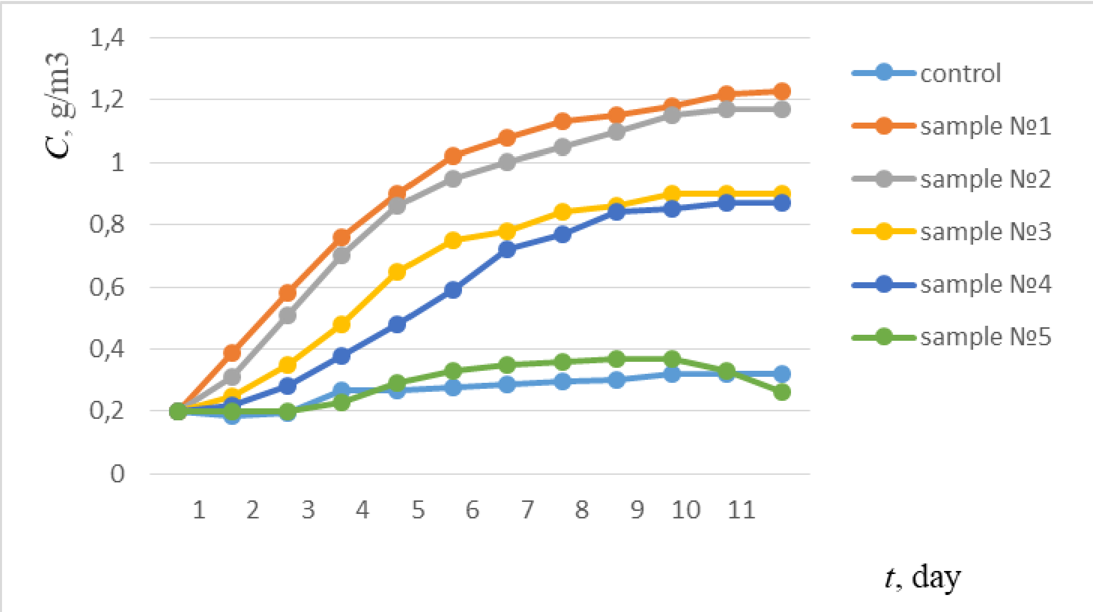

Fig. 3. Combined effect on the growth of microalgae biomass of HS^- and NH_4^+ ions

The defining parameter that characterizes the growth of microalgae δμ is the specific growth rate:

$$\delta_k=\delta C_1/C\times\delta t, \quad (1)$$

where C is the concentration of microalgae, δμ is the specific growth rate or specific growth rate (s^{-1}).

We determined the growth rate from the kinetic equation:

$$\delta C/\delta t=\mu\times C. \quad (2)$$

According to equation (2), the growth factor characterizes the relative increase in the density of microalgae per time unit. If δμ remains unchanged for a particular time, then such an increase is called exponential, and the corresponding period is the exponential phase of growth.

Integrating equation (2), we find a constant integration provided that at the initial time t = 0, there is an initial density of microalgae cells C0.

$$C=C_0\times\exp(\mu t). \quad (3)$$

Since the logarithmic dependence of the concentration of microalgae cells on time during the exponential growth is a linear dependence, it makes it possible to determine the growth coefficient μ as the tangent of the angle of inclination of the experimental line (Manakov, 1990). Therefore, substituting the experimental data in equation (3), we obtain the dependences *ln C*=f(*t*), which are shown in Fig. 4.

After mathematical processing of the results of experimental research and the obtained calculated data, the highest value of the growth factor has Sample 1, μ = 0.1107 d^{-1} (Fig. 4) and Sample 2, μ = 0,1086 (Fig. 4, Table 1). The values of the growth coefficients for other samples are presented in Table 1.

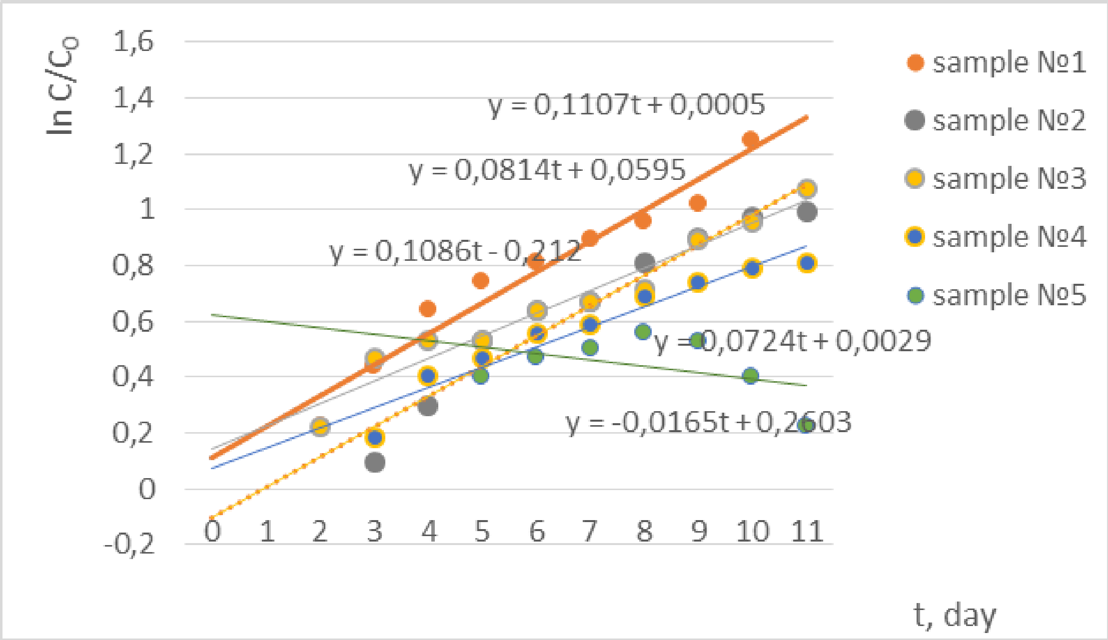

Fig. 4. Dependence of the change in the logarithm of the microalgae content on time (at the corresponding concentrations of activators NH_4^+ and the inhibitor HS^-)

Table 1

Experimental data and calculated values

Sample	*μ growth coefficient, d^{-1}*	*HS – vol. % concentration, mg/m^3*	*NH_4^+vol. % concentration, mg/m^3*
Control	0.0292	–	–
Sample 1	0.1107	0.5	1.5
Sample 2	0.1086	0.5	1.0
Sample 3	0.0814	1.0	1.5
Sample 4	0.0724	1.0	1.0
Sample 5	-0.0165	2.5	2.0

4. Conclusion

It was found that sulfide ions HS^- inhibit the growth of Chlorella Vulgaris regardless of the initial concentration of microalgae. Over time, sulfides are oxidized to sulfates, which stimulates proliferation because they are the main assimilative form of sulfur.

The optimal concentration of HS^- sulfide ions in the cultivation medium of Chlorella Vulgaris is the concentration corresponding to 0.5–1.0 vol. % of hydrogen sulfide in biogas.

The use of microalgae Chlorella Vulgaris for purification of biogas from hydrogen sulfide is possible by diluting biogas, in particular ammonia, to achieve optimal values of hydrogen sulfide concentration.

In the future, the obtained biomass of microalgae Chlorella Vulgaris should be investigated by thermal analysis for the feasibility of using it as biofuel.

References

Awe, O. W., Zhao, Y., Nzihou, A., Nzihou, A., Minh, D. P., & Lyczko, N. (2017). A Review of Biogas Utilisation, Purification and Upgrading Technologies. *Waste Biomass Valor*, *8*. 267–283. doi: https://doi.org/10.1007/s12649-016-9826-4

Bailón Allegue, L., & Hinge, J. (2014). *Biogas upgrading Evaluation of methods for H_2S removal*. Danish Technological Centre. Copenhagen.

Dyachok, V., Huhlych, S., Katysheva, V., & Mandryk, S. (2021). About the Optimal Ratio Inhibitor and Activators of Carbon Dioxide Sorption Process by Using Chlorophyll-synthesizing Chlorella microalgae. *Journal of Ecological Engineering*, *22*(5), 26–31. doi: https://doi.org/10.12911/22998993/135900

Chlorella in sewage treatment. (2020). Retrieved from https://hlorella.jimdo.com/

Dyachok, V., Huhlych, S., Katysheva, V., & Mandryk, S. (2017). Absorption of carbon dioxide from a mixture of air with sulfur dioxide (in Ukrainian). *Naukovi Pratsi Onakht*, *81*(1), 59–65. Retrieved from http://journals.uran.ua/swonaft

Dyachok,V. V., Mandryk, S. T., Huhlych, S. I., & Slyvka, M. M. (2020). Study on the impact of activators in the presence of an inhibitor on the dynamics of carbon dioxide absorption by chlorophyll-synthesizing microalgae. *Journal of Ecological Engineering*, *21*(5), 189–196. doi: https://doi.org/10.12911/22998993/122674

Kaltschmitt, M., Hartmann, H., & Hofbauer, H. (2016). *Energie aus Biomasse. Grundlagen, Techniken und Verfahren*. 3rd ed. Berlin: Springer. Retrieved from https://www.openagrar.de/receive/openagrar_mods_00022991

Manakov, M. N., & Pobedimskiy, D. H. (1990). *Theoretical bases technology of microbiological productions technology*. Ahropromisdat.

67 % of greenhouse gas emissions are caused by energy and burning of fossil fuels (in Ukrainian). (2020). Ofitsiyhyy portal Ministerstva zakhystu dovkilla i pryrodnykh resursiv Ukrainy. Retrieved from: https://mepr.gov.ua/news/34553.htm.

Poltorak, O. M., & Chukhray, O. S. (1972). *Physicochemical bases of enzymatic catalysis*.

Zolotaryova, O. K., Shnyukova, Ye. I., Syvash, O.O., & Mykhaylenko, N. F. (2008). *Prospects for the use of microalgae in biotechnology*. In: O.K. Zolotaryovoa (Ed.) Alterpres, 234.