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# Modeling of Hydrogen Sulfide Removal Under Biomethane Production in the Concept of Renewable Energy Potential Growth of Ukraine

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# Modeling of hydrogen sulfide removal under biomethane production in the concept of renewable energy potential growth of Ukraine

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**Abstract.** Today, the global trend in the development of renewable energy sources is the implementation of integrated processing of organic waste with the production of biogenic gases such as biomethane. In this case, an essential focus is the study of biogas purification processes to methane. This paper focuses on the process of modeling biochemical purification of biogas from hydrogen sulfide to develop the direction of biomethane production. Simulation of hydrogen sulfide bio-oxidation process with the use of granulated carrier based on phosphogypsum was conducted using experimental data from previous studies to verify the adequacy of the proposed mathematical model. Thus, to implement the process of phosphogypsum utilization in technological systems of biogas purification, it is important to consider the level of bioactivity in the immobilization of bacteria on the loading surface of phosphogypsum and the degree of biotransformation of phosphogypsum components in the oxidation of carbon dioxide and hydrogen sulfide impurities to achieve the highest ecological effect. Also, the use of overlay visualization allowed to form the main clusters of development of research potential in the field of biogas technologies for Ukraine.

## 1 Introduction

Currently, there is a rapid development of bioenergy worldwide, in particular, the technology of production of biogenic gases for energy purposes [1]. Such countries as Germany and Austria have become the flagships of development in Western Europe, the bioenergy potential is actively developing in the Scandinavian countries (Sweden, Norway) and the United States. Relevant is the problem of the development of renewable energy potential for Ukraine [2,3] (Fig.1).

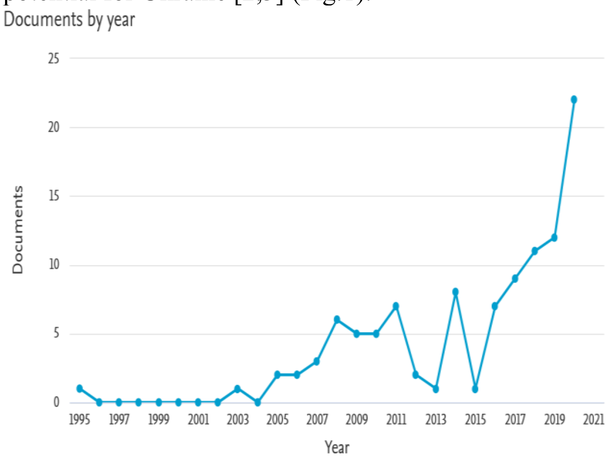


**Fig. 1.** Publishing trends (number of papers) in the field of biogas technologies research of Ukrainian scientists (using the Scopus database)

When analyzing the publication activity on the query biogas technologies and biomethane production in the Scopus database was highlighted key areas of publications of Ukrainian scientists in highly rated journals, which are associated with bioprocesses of biogas production and waste recycling (Fig. 2 and 3) [4-6]. Thus, the sphere of implementation of scientific research in Ukraine also has significant potential for development and is integrated into the world scientific metrics in the field of bioenergy.

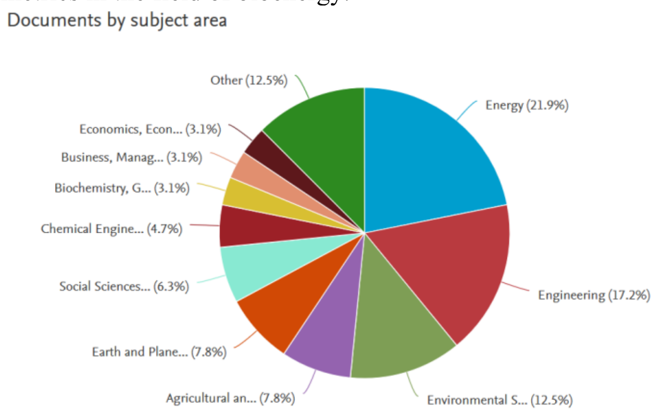


**Fig. 2.** Directions of publication activity by field of biogas technologies research (using the Scopus database)

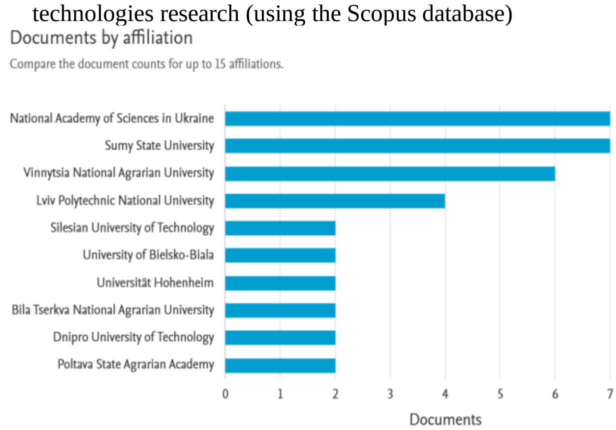


**Fig. 3.** Affiliation with the leading scientific and educational organizations of Ukraine according to the Scopus database in the field of biogas technology development

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The priorities of the new energy strategy of Ukraine until 2035 according to [7] related to bioenergy are as follows:
- promoting the creation of competitive biomass markets.
- support for implementation of cogeneration projects at CHPPs and cogeneration with biofuels;
- creation of conditions for the creation of logistic system and infrastructure for collection of biomass and its further transportation;
- providing centralized heating systems with energy from renewable sources (bio-pellets, household waste, etc.);
- increasing the share of energy exchange in % of domestic consumption, including other fuels, from 10% in 2015 to 60% in 2035.

An important direction is also the introduction of integrated processing of organic waste with the production of biogenic gases such as biomethane. In this case, an essential focus is the study of biogas purification processes to methane.

Under our previous studies [8,9] we consider phosphogypsum as an acid-resistant mineral carrier, and besides, it is a source of macro- and microelements for the development of necessary ecological and trophic groups of bacteria. Phosphogypsum entering the environment of life activity of microorganisms becomes a source of nutrition and stimulates metabolic processes of a bacterial cell due to a list of elements necessary for its life activity.

The model of the influence of the main components of phosphogypsum on the vital functions of microorganisms is presented in Fig. 4. For its formation, we used data from previous studies [8,9] and electronic bioinformation databases of the Kyoto Encyclopedia of Genes and Genomes (KEGG) and Metabase of Bacterial Diversity (BacDive).

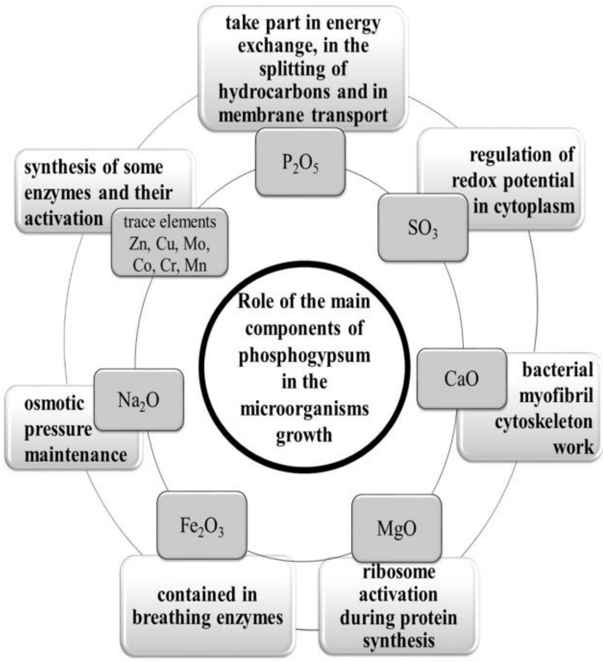


**Fig. 4.** Role of main phosphogypsum components in microbial activity

The annually worldwide production of phosphogypsum is possibly up to 100 million tons [10]. The use of the modified granulated phosphogypsum will make it possible to expand the scope of its use in biochemical purification processes, which is relevant not only for Ukraine, but also throughout the world.

It should be noted, at realization of biogas technologies the special attention is given to quality of biogas and, in particular, to the content of methane, carbon dioxide and other impurities, such as hydrogen sulfide.

Due to the complexity of biochemical reactions, and the presence of inhibitors or hard-to-degrade compounds in the waste, a detailed study of the kinetics is necessary to understand and optimize the process. Vavilov [11] developed mathematical models describing the kinetics of acidogenesis, ethane-degrading acetogenesis, butyrate-degrading acetogenesis, acetoclastic methanogenesis, hydrogenotrophic methanogenesis, bacterial degradation. Gutiérrez Ortiz and Aguilar POllero (2014) provided a methodology for dynamically estimating the total mass transfer coefficient as well as the most appropriate isotherm for a stream containing treated sewage sludge for biogas desulfurization, which requires still evaluating the transition from laboratory studies to industrial applications [12]. The model was verified by comparing the data obtained with experimental data from the literature. Khanongnuch (2019) compared Michaelis-Menten fermentation equations, first- and second-order kinetics of substrate decomposition of cellulose particles of known sizes [13]. The research by Pokorna-Krayzelova et al. (2018) shows that few authors have quantified the kinetics of chemical and biochemical oxidation of sulfides in a single oxygen-limited system. Moreover, the publicly available data are still not consistent, and more specialized measurements are still needed to independently calibrate mathematical models [14].

Accordingly, for wide implementation of technologies of biomethane production, it is important to simulate the processes of gas purification with removal of impurities.

However, the growth patterns of bacteria on low-soluble mineral substrate are still practically unstudied. For example, phosphogypsum; in addition, there are practically no data on mathematical modeling and investigation of the biochemical desulfurization process during solid-phase fermentation.Thus, this paper focuses on the process of modeling biochemical purification of biogas from hydrogen sulfide to develop the direction of biomethane production.

This paper focuses on the process of modeling the biochemical purification of biogas from hydrogen sulfide during the biofilm growth on phosphogypsum granules as part of the development of the concept of biomethane production.

## 2 Materials and methods

Under implementing the mathematical model, we used the values of constants given in Table 1.

**Table 1.** Constants needed for the software implementation of the mathematical model [15]

| Constanta | Value | Unit of measure |
|---|---|---|
| $Y_{X/S}$ | 0.093 | mg/mg |
| $\mu_m$ | 0.037 | $d^{-1}$ |
| $\lambda$ | 0.031 | $d^{-1}$ |

**Table 2.** Symbolic names for program development

| Initial designation | Symbolic name | Explanation |
|---|---|---|
| $F_g$ | F | input consumption of gas flow containing hydrogen sulfide, $dm^3$ / min |
| $\mu_m$ | m_max | the specific growth rate of thiobacteria, $h^{-1}$ |
| $V_{gpg}$ | V | specific layer volume of granulated phosphogypsum, $dm^3$ |
| $C_n$ | Cn | the minimum value of hydrogen sulfide concentration, ppm |
| $C_k$ | Ck | the maximum value of hydrogen sulfide concentration, ppm |
| $\Delta C$ | dC | hydrogen sulfide concentration value change, ppm |
| $\alpha_B$ | *a* | oxidative capacity of biofilm, g / $cm^3$ h |
| t | t | contact of the gas flow with the mineral carrier from phosphogypsum, h |
| $\xi_{gph}$ | L | the biochemical capacity of loading from phosphogypsum, $gH_2S$ / $cm^3$ |
| $C_{H2S}$ | Chs | the actual concentration of hydrogen sulfide, ppm |
| $\lambda$ | l | inactivation rate constant, $d^{-1}$ |
| e | e | natural constant |
| $Y_{X/S}$ | Y | economic coefficient of thiobacteria biomass yield by substrate - hydrogen sulfide |

Fig. 5 shows a simplified algorithm for the simulation process. The computational model was carried out using the programming language $C^{++}$ in the integrated environment Borland $C^{++}$, which is designed to describe a wide range of tasks and contains mechanisms for controlling the computational process and working with data, optimally suited for the task.

The output data were determined following the biochemical conditions of the biomethane generation process (Table 3).

In this case, the value of C changed in the range, ppm: 250, 400, 550, 700, 850.

**Table 3.** Initial data for modeling

| Initial condition | Value | Unit of measure |
|---|---|---|
| $\tau$ | 1.5 | h. |
| $F_g$ | 0.23 | $dm^3$/min. |
| $V_{gph}$ | 1.8 | $dm^3$ |

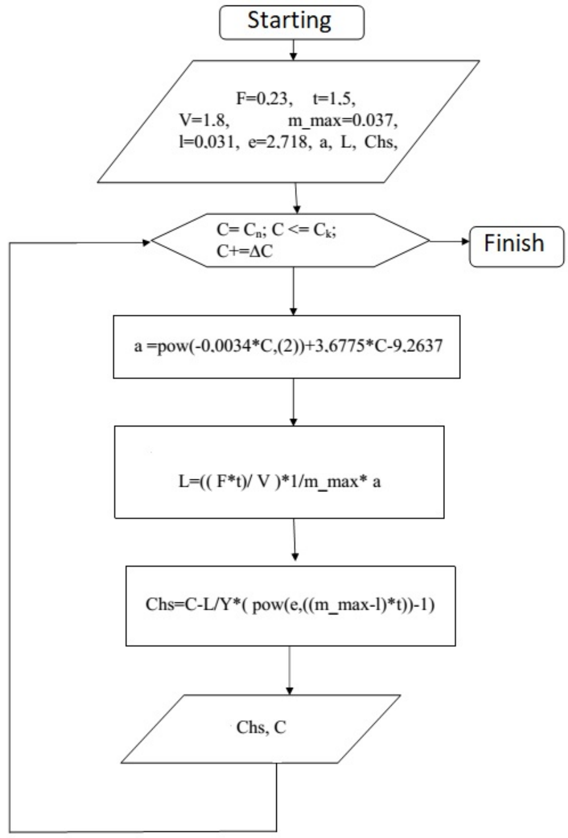


**Fig. 5.** Simulation algorithm

To calculate the correlation coefficient between the experimentally determined values of hydrogen sulfide concentration and the values obtained in the simulation, MS Excel program package with the built-in CORREL function was used. Also, special visualization software (VOSViewer v.1.6.15) was used to build a map to visualize the clusters of biogas production in Ukraine.

## 3 Results and Discussions

### Modeling of hydrogen sulfide removal from biogas for biomethane production

Mathematical modeling of kinetics of hydrogen sulfide conversion by sulfur-oxidizing microorganisms in the process of phosphogypsum utilization assumptions have been put forward: the entire working volume of the biofilter is uniformly filled with phosphogypsum load; concentrations of mineral substrate (phosphogypsum) and biofilm at each point of the biofilter are equal; substrate concentration and the total number of cells are linearly related, the change in hydrogen sulfide concentration ($C_{H_2S}$) when passing the maximum in the number of viable cells N (at $\mu_m = \frac{1}{N} \cdot \frac{dN}{d\tau}$ = const) gives exponential function and finds dependence on biochemical properties of phosphogypsum load ($\xi_{gph}$). The mathematical model of the developed biodesulfurization process using phosphogypsum loading is based on the classical Mono model, widely used in the optimization of biotechnological systems.

Important for analyzing the efficiency of using phosphogypsum as a mineral carrier for immobilization of microorganisms is to evaluate the biochemical capacity of phosphogypsum loading, taking into account the sorption processes on its surface and the uniform distribution of hydrogen sulfide gas flow. Then the behavior of hydrogen sulfide concentration in time and change in the value of biochemical capacity of phosphogypsum loading can be described by the system of ordinary differential equations:

$$\frac{dC_{H_2S}}{d\tau} = \mathrm{C} - \frac{\xi_{gph}}{Y_{X/S}} \times \left(e^{(\mu_m - \lambda)\tau} - 1\right), \quad (1)$$

$$\frac{d\xi_{gph}}{d\tau} = \frac{F_g \times \tau}{V_{gph}} \times \frac{1}{\mu_m} \times \alpha_B \quad (2)$$

where $\xi_{gph}$ is the biochemical capacity of loading from phosphogypsum, $gH_2S$ / $dm^3$; C is the concentration of $H_2S$ in the biogas stream, g / $dm^3$; $Y_{X/S}$ is economic thiobacteria biomass yield factor by substrate - hydrogen sulfide; $\mu_m$ is the specific thiobacteria growth rate, $h^{-1}$; λ is inactivation rate constant, failure rate, leading to loss of thiobacteria cells' ability to reproduce, $h^{-1}$; $F_g$ is input gas flow containing hydrogen sulfide, $dm^3$ / min; τ is contact time, min.; $V_{gph}$ is a specific layer volume of modified phosphogypsum granules in biofilter or bioscrubber, $dm^3$; $\alpha_B$ is the oxidative capacity of biofilm, g / $dm^3$ h.

In the process of metabolic activity of sulfur-oxidizing bacteria, there is consumption as a mineral substrate of phosphogypsum. Therefore, when calculating the value of the reduction of hydrogen sulfide concentration in the gas stream in equation (1) was introduced an indicator characterizing the biochemical capacity of phosphogypsum loading.

In expression (2) when describing the biochemical capacity were taken into account parameters affecting the intensity of sorption on the surface of granules, and biochemical activity, which is characterized by the specific growth rate of bacteria and the oxidative capacity of biofilm, which was determined experimentally.

Thus, expression (2) takes into account the most important conversion parameters, without which it is impossible to predict the biochemical component of purification efficiency, since we consider biochemical removal of impurities from biogas as one of the main direction of research on biomethane production. With further development of complex technical solutions, the model can be expanded and optimized for a number of other parameters.

As can be seen from the graph (Fig. 6) the oxidative capacity of biofilm $\alpha_B$ changes with changes in the concentration of hydrogen sulfide in the gas stream.

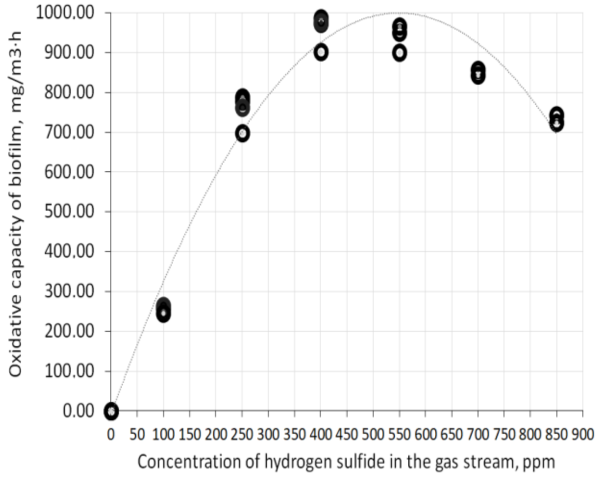


**Fig. 6.** Biofilm oxidative capacity curve. According to the experimental data from [9].

Experimental data of dependence of biofilm oxidative capacity ($\alpha_B$) on the concentration of hydrogen sulfide (C) in biogas can be approximated by regression equation:

$$\alpha_B = -0.0034C^2 + 3.6775C - 9.2637 \ (R^2 = 0.9737) \quad (3)$$

A curve was obtained (Fig. 7), which corresponded to the theoretical dynamics of hydrogen sulfide reduction and had a good coincidence with the experimental data.

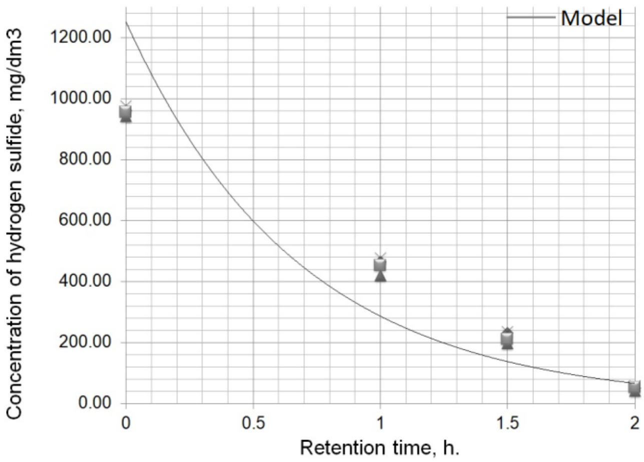


**Fig. 7.** Change of hydrogen sulfide concentration in biogas with time. Comparative analysis of experimental data and results of mathematical modeling (r = 0.923).

The greatest decrease in hydrogen sulfide concentration occurred in the second half-period of treatment from 0.5 to 1.0 hour, which corresponded to the stabilization of the development of the bacterial film on the surface of modified phosphogypsum granules after the end of the adaptation period. Thus, to implement the process of phosphogypsum utilization in technological systems of biogas purification, it is important to consider the level of bioactivity in the immobilization of bacteria on the loading surface of phosphogypsum and the degree of biotransformation of dihydrate phosphogypsum in the conversion of carbon dioxide and hydrogen sulfide impurities to achieve the highest ecological effect.

Thus, such species of *Thiobacillus* sp. as *Th. Intermedius* and *Th. Permetabolis* grow under autotrophic conditions, which is associated with the ability of these bacteria to use carbon dioxide to form cell components:

$$CO_2 + H_2O + Enzymen \rightarrow \left[CH_2O\right] + O_2 \tag{4}$$

Bacterial growth reaches a maximum ($3.5 \cdot 10^{10}$ CFU/g) with maximum removal of $H_2S$ (95.34 %) when supported at pH = 5.0 and contact time of 10 hours [9]. There is a stratification of microbial groups with the development of a zone of facultative aerobiosis and anaerobiosis in the inner bioactive layer of modified phosphogypsum granules.

## 4 Conclusions

A comprehensive approach to modeling the removal of hydrogen sulfide from biogas and the analysis of the prospects for implementation of biomethanogenesis processes in Ukraine was described.

Simulation of hydrogen sulfide bio-oxidation process with the use of granulated carrier based on phosphogypsum was conducted using experimental data from previous studies to verify the adequacy of the proposed mathematical model.

Further research will focus on the experimental work of the integrated stage-by-stage production of biohydrogen and biomethane with the production of environmentally safe digestate.

## 5 Acknowledgments

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