DOI: 10.2429/proc.2012.6(2)068 2012;6(2)

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CHANGEABILITY MODEL OF THE BOG ORE HYDROGEN SULFIDE SORPTION ABILITY

MODEL ZMIENNOŚCI ZDOLNOŚCI SORPCYJNEJ RUDY DARNIOWEJ WZGLĘDEM SIARKOWODORU

Abstract: Basing on long-standing cyclic measurements of sludge-originated biogas composition and considering statistical analysis of their results, a regression model describing time variation of biogas desulfurization using bog iron ore has been developed. The model was verified by theoretical calculations and results from laboratory examinations of the sorbent. It was also used to estimate the depletion time and sorption capacity of the bed and to determine the demand index for bog ore.

Keywords: sewage sludge, fermentation, biogas, desulphurization, statistical analysis, forecasting

Having regard to the boom forecasted for biogas plants [1, 2], it would be necessary to develop biogas treatment methods, especially in the context of its industrial combustion. Removal of sulphur hydrogen, which creates threat for instrumentation and environment, is among one of the most important stages in biogas treatment process [3]. Due to availability of the sorbent and low related capital and operating costs, bog ore, the mineral including iron compounds reacting with H_2S, is commonly used for this purpose in Poland. However a barrier for its further effective use may be the lack of experimental data about its sorption capacity, mechanisms of sorption and the possibilities of its intensification.

The mathematical model of time variability of biogas desulfurization efficiency using bog ore was developed basing on long-standing, quarterly investigations of biogas generated from sludge in *Wroclaw Sewage Treatment Plant* (WSTP) [4]. It was then used to calculate the bed sorption capacity and to determine the sorbent demand index per 1,000 m^3 of biogas. The results from model calculations were compared with sorption capacity calculated theoretically and with the results of laboratory examinations.

This paper is continuation of the previous examinations [5]. Information about analytical methods is given in items [4-7] while that of generation and treatment of biogas under investigation - in [4, 8, 9].

Biogas desulphurization using bog ore

For the bog ore could be the H_2S sorbent, it shall be made free of minus 200 μm grain size fraction, organic substances and carbonate minerals. Activation of the ore consists in calcining, fluffing (*eg* by adding sawdust) and alkalizing with calcium hydroxide, sodium hydroxide or sodium carbonate [10].

Mechanism of biogas desulfurization using bog ore is strongly dependent on pH value. Alkaline medium is more favourable as it generates Fe_2S_3 which faster reacts with oxygen. This facilitates regeneration consisting in oxidizing ferrous sulpfide(III) back to the active

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form of ferrous oxide(III). In acid environment, the free sulphur coming out in a process, blocks the pores and faster deactivates active iron compounds.

Two parallel cylindrical desulfurization grid-type units with four filtration baskets are used for biogas desulfurization at Wroclaw Sewage Treatment Plant. The units are filled with bog ore from Strzyzow deposits near Kalisz, prepared according to the recipe of the Institute of Chemistry, Petroleum and Coal Technologies at Wroclaw University of Technology. Raw ore was modified by addition of alkaline activators (NaOH, Na_2CO_3) and fluffing agents in form of sawdust.

Statistical analyze

The model was developed on the basis of own 30 tests of the biogas desulfurization efficiency (η), made in the years 2002-2009, and dates of bed replacement. Investigations included two desulphurizers.

Three types of trends were examined: second degree polynomial ($\eta = 0.00225 \cdot \tau^2 - 0.726 \cdot \tau + 100$), linear ($\eta = -0.374 \cdot \tau + 100$) and exponential ($\eta = 100 \cdot \exp(-0.00682 \cdot \tau)$), to determine the H_2S removal efficiency versus sorption time (τ).

Reliability of regressions under analysis for describing time variability of desulfurization efficiency was evaluated using standard tools of statistical analysis (Table 1). For comparison purposes, the version of ideal relation between calculated and measured efficiencies was presented.

Table 1

Values of model estimation statistical indicators

Indicator	**Reference value ($\eta_{oi} = \eta_{pi}$)**	**Function**		
		Polynomial II deg.	**Linear**	**Exponential**
Correlation coefficient R	1	0.78	0.90	0.95
Deviation of averages D_C [%]	0	7.57	3.91	1.42
Relative deviation of averages W_C [%]	0	11.26	5.81	2.11
Average deviation B_C [%]	0	11.34	10.6	6.9
Relative average deviation O_C [%]	0	16.86	15.77	10.31

The dissipation diagram (Fig. 1) was made to evaluate the degree of overrating or underrating the results also. The points with coordinates (η_{pi}, η_{oi}) were introduced into the diagrams. Theoretical points should lie along a straight line inclined at 45º and starting from the origin of coordinate system. The degree of dispersion with respect of this line is the measure of model accuracy.

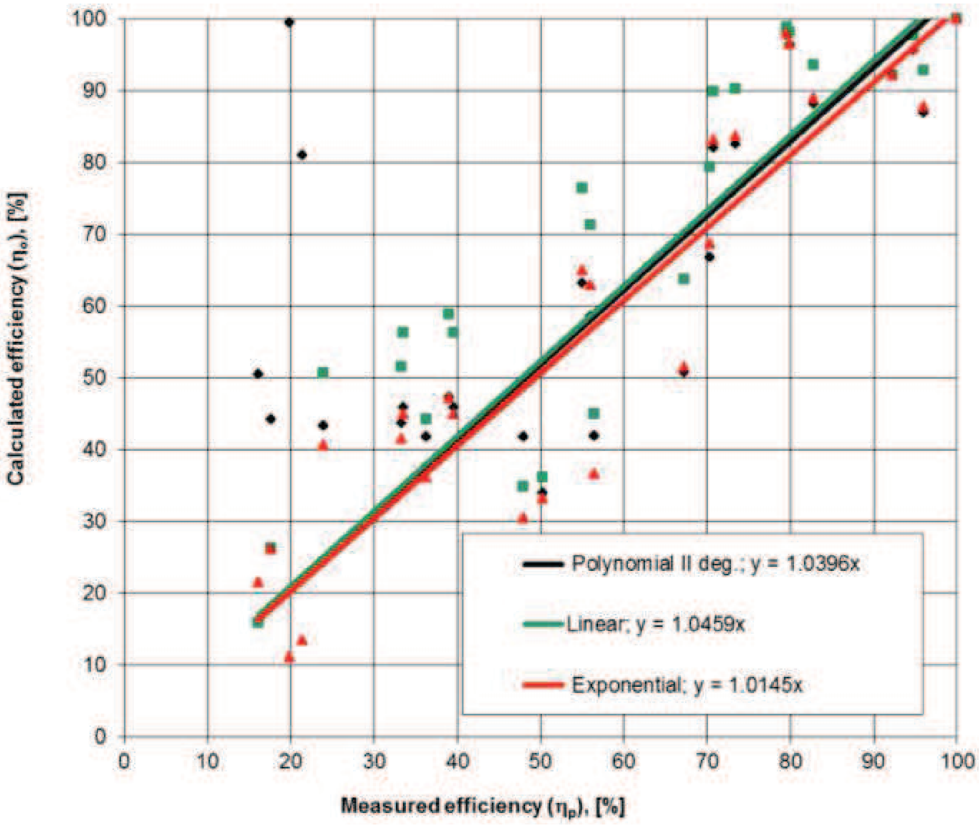

Fig. 1. Diagram of dissipation

Results and discussion

Upon analyzing the indexes of statistical evaluation for regression versions under consideration (Table 1) and the dissipation diagram (Fig. 1), the exponential model was selected for further calculations. It was used to find the trend lines of H_2S absorption efficiency decline with sorption time which lines were then included into particular measurement series (Fig. 2). Trend lines for particular measurement series put on measurement points show no essential dependence between the sorption capacity decline and absorbed load of H_2S. Hence, it appears that apart from hydrogen sulphide there are other factors which deactivate the ore. Potentially belongs to them: acidification of reaction environment by CO_2 (elementary sulphur, which precipitates under such conditions, blocks the pores and impedes H_2S access to active iron compounds [11]), oxygen existing in biogas, which causes that sulphides are oxidized to elementary sulphur [12], binding F^{3+} and Fe^{2+} iron by CO_2, leads to creating iron carbonates and bicarbonates which block the pores.

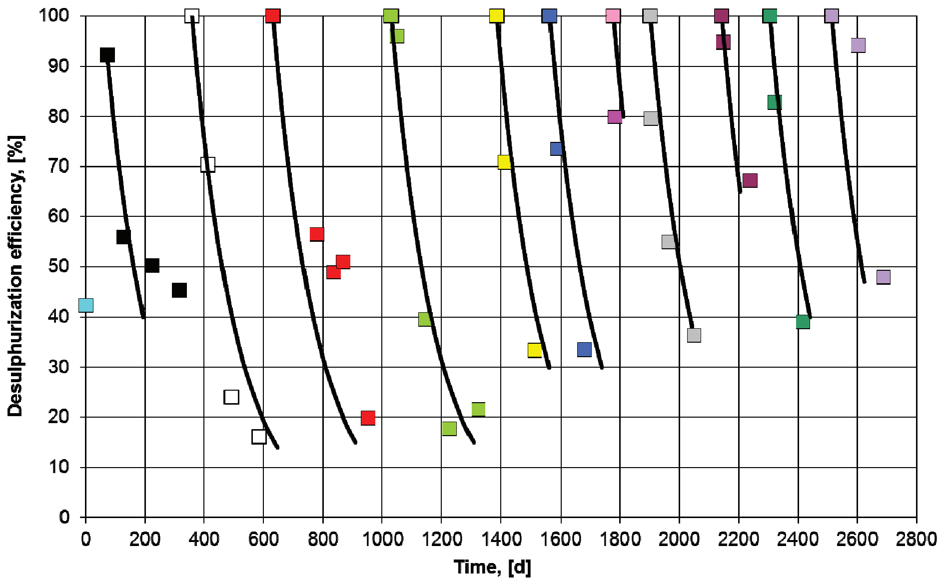

Fig. 2. Time changeability of H_2S removal efficiency

Verification and usage of the model

Model results of bed depletion time were compared with those from stoichiometric calculations and those from laboratory testing. The assumptions were that:

- the reaction of H_2S binding proceeds according to equations:
  $Fe_2O_3 + 3H_2S \rightarrow Fe_2S_3 + 3H_2O$, $2NaOH + H_2S \rightarrow Na_2SO_3 + 2H_2O$
- concentration of H_2S in raw biogas, desulfurization efficiency, volumetric flow of biogas, volume and apparent density of the bed correspond to averaged values of these parameters for both desulfurization units over the full examination time (respectively: 153.7 mg/m_n^3, 54.5%, 219 m_n^3/h, 3.4 m^3 and 941 kg/m^3),
- bed humidity and content of Fe_2O_3 and NaOH in the bed are at averaged levels from laboratory testing (respectively: 50, 3.38, 22.91% d.m.).

In theory, considering exclusively the reactions with Fe_2O_3 (m_{H2S1}) and NaOH (m_{H2S2}), a single desulfurization unit can bind 258.4 kg H_2S. Hence, theoretical time of bed depletion, corresponding to average mass stream of absorbed H_2S equals 587 d.

According to laboratory results, the sorbent under consideration can absorb at least 0.1878 kg S/kg of bed dry matter, which corresponds to the time of complete exhaustion 725 d. But, according to the regression model proposed, while assuming the minimum final efficiency $\eta = 5\%$, the maximum time of total bed exhaustion can be evaluated at 439 d. Using the suggested model, it was also determined the expected efficiency of desulfurization units at the moment of bed replacement, which - as averaged for all measurement series - was c. 20%, practical (maximum) operating time of the bed (235 d) and practical absorbing power of bog ore (0.059 kg S/kg d.m.). On this grounds, the bog ore consumption index of purified biogas was estimated (0.0028 m^3/1000 m_n^3 of biogas).

Conclusions

Calculations made for statistical coefficients proved that the exponential model provides the best representation of time variability of bog ore sorption capacity for H_2S. The sorption capacity found from this model, corresponding to practical operating period of the bed, is 0.059 kg S/kg of dry matter which represents about 30% of the capacity attained in laboratory (the difference may result from difficulties in maintaining the optimum operating conditions, such as pH value, temperature and humidity, for desulfurization units under real conditions).

The demand index for bog ore evaluated by the model proposed is c. 0.003 $m^3/1000\ m_n^3$ of biogas, *ie* 2.6 $kg/1000\ m_n^3$.

For the technology of sewage treatment and biogas treatment under consideration, the total time of bed depletion calculated by the model developed is 439 days while practical period of bed operation (*ie* till the efficiency is 20%) - 235 days.

Sulphur hydrogen is neither the just one nor the most important factor of bog ore deactivation. It is the carbon dioxide contained in biogas which seems to be the main factor of sorption capacity decline. Also the sawdust added to fluff the bed and oxygen present in biogas have an adverse impact on chemical mechanisms of H_2S absorption.

Considering the good points of biogas desulfurization with bog ore (*ie* availability and low purchase costs of the sorbent, simple operation and high availability factor of the plant) and its drawbacks (relatively low and time-variable efficiency of H_2S removal, arduous replacement of the bed, problems with waste disposal, limited potential of process automation and control, lack of market-available product with uniform and standardized properties, *eg* granulate) and also the effects attained (in general, biogas meets, after desulphurization, the specifications demanded by gas motor manufacturers), a statement could be made that, under Polish conditions, biogas desulfurization with bog ore is justified mainly due to economical reasons. However, the method needs further studies. Many authors, like [13-15], draw attention to insufficient knowledge about sorption properties of bog ores and the sorption mechanisms as well.

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MODEL ZMIENNOŚCI ZDOLNOŚCI SORPCYJNEJ RUDY DARNIOWEJ WZGLĘDEM SIARKOWODORU

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Abstrakt: Na podstawie wieloletnich, cyklicznych pomiarów składu biogazu powstającego z osadów ściekowych, wykorzystując analizę statystyczną wyników, opracowano model regresyjny, opisujący czasowy charakter zmienności skuteczności odsiarczania biogazu za pomocą rudy darniowej. Model został zweryfikowany za pomocą obliczeń teoretycznych i wyników badań laboratoryjnych sorbentu. Za jego pomocą oszacowano czas wyczerpania i pojemność sorpcyjną złoża oraz wyznaczono wskaźnik zapotrzebowania na rudę darniową.

Słowa kluczowe: osad ściekowy, fermentacja, biogaz, odsiarczanie, analiza statystyczna, prognozowanie