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EFFECT OF AQUA KEM GREEN CHEMICALS ON TECHNOLOGICAL EFFECTIVENESS OF GASIFICATION OF PLANT BIOMASS

Development of sailing tourism is contributes to degradation of the natural environment, waters of lakes and rivers in particular. Wastewaters produced on sailboats and yachts and deposited in their chemical toilets are usually discharged directly to aquifers, with a minor part being discharged to collectors for these are located in a few ports only. Thus, it seems indispensable to develop a complex system of collection and neutralization of such wastewaters. It is, however, a difficult process for it requires solving both logistic and technological problems. One of the technological problems may involve adopting an optimum method for neutralization of the wastewaters that usually contain chemical agents for the removal of unpleasant odours, e.g. Aqua Kem Green type. A solution to this problem may be co-gasification of wastewaters from sailboats with plant biomass in the fermentation process in a biogas works.

1. INTRODUCTION

Poland is a country with great natural wealth of lakes, accumulated mainly in the Great Lakeland of the Warmia and Mazury Region. These beautifully located areas are highly attractive from the recreational point of view and serve the constantly developing tourism, e.g. sailing. Unfortunately, this development is becoming the cause of advancing degradation of the natural environment. Cases of discharging wastewaters from chemical toilets of sailboats directly to lake waters recently increased. A lack of system solutions for the collection of produced wastewaters or insufficiently stipulated requirements for chemical toilets exploitation additionally contribute to long-lasting degradation of this outstanding landscape and deterioration of water purity.

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Worthy of notice is the fact that each year the Great Masurian Lakeland is visited by over 50 000 sailors, which means that 10 000–12 500 sailboats and yachts are sailing in this area. Ca. 40% of the latter are equipped in chemical toilets [1]. The use of chemical toilets involves application of chemicals that, among others, assure neutralization of unpleasant odours. Contemporarily, the chemical agents used in chemical toilets are produced based on bronopol.

An exceptionally high activity of bronopol (2-bromo-2-nitropropane-1,3-diol) has been observed especially against strains of Gram-negative bacteria. It has become a highly popular bactericide (as a substitute of formaldehyde) not only in toilet preparations but also in the cosmetic and pharmaceutical industry.

One of such chemicals is Aqua Kem Green. Unfortunately, the mixture of fecal matter and chemical substances produced upon the use of this type of agents requires appropriate treatment. Nowadays, treatment of wastewaters from yachts proceeds in wastewater treatment plants located on the area of the Great Masurian Lakeland. However, managers of these plants often refuse to collect sewages from chemical toilets both from yachts, coaches or camping sites. These plants are operating based on the method of activated sludge, therefore an additional load of discharged impurities increases their demand for energy that is necessary for the exploitation of aeration tanks. They are also highly overloaded with additional discharges of wastewaters in the summer season. What is more, microflora of the activated sludge is susceptible to toxic substances occurring in wastewaters. Hence, a good solution to this problem appears to be making use of agricultural biogas works or selected fermentation tanks of municipal wastewaters treatment plants. Anaerobic biodegradation of sewages has a number of advantages [2]. It results in the production of sewage gas containing a high-energy component – methane, whilst microorganisms of anaerobic sludge are capable of decomposing many toxic chemical compounds [3, 4].

Biogas works are usually located on rural areas with easy access to fermentation substrate. The Great Masurian Lakeland is, undoubtedly, the area used for farm production; hence a vast increase is expected here in biogas production investments. Costs of purchase of fermentation substrate may be reduced by means of mixing plant biomass with wastewaters. In this case, the mixing of, e.g. maize silage with wastewaters from sail boats seems advisable. This will enable diluting chemical substances contained in wastewaters from chemical toilets, reducing sewage load in the neighbouring wastewater treatment plants, and most of all will make the wastewaters a source of energy. Finally, this means development of economic mechanisms that will allow one to establish a network of effective collectors for chemical toilets.

The objective of this study was to find the optimum dose of bronopol containing chemicals that would neither contribute to inhibition of fermentation processes nor disturb significantly the activity of a biogas works.

2. EXPERIMENTAL

The experiment was conducted at the laboratory of the Department of Environment Protection Engineering at the University of Warmia and Mazury in Olsztyn. It was conducted in two variants by the same method. Difference was the use of various loading of the active tank volume with feedstock of organic compounds. In the former variant assays were carried out with the level of 2.5 kg o.d.m./m^3 and in the latter – 5.0 kg o.d.m./m^3

Analyses were made for the effect of the dose of Aqua Kem Green chemicals at various loadings of tanks with a load of carbon compounds on the final technological effects of the methane fermentation process. The objective of this experiment was to determine the dose of the bronopol containing chemical agents that would not disturb the fermentation process which has a direct impact on biogas production.

Prior to exact fermentation with the use of a system of respirometers, a substrate (maize silage) was appropriately conditioned and prepared (it was subject to 10 min mixing and chopping with a type 3 blixer (Robot Coupe) for proper disintegration).

The tested doses of Aqua Kem Green chemicals containing bronopol were administered into measuring devices that enable determining the degree of degradability of organic matter as well as monitoring the quantity and composition of biogas produced. In the experiment, use was made of Oxi-Top Control respirometric kits by the WTW Company which consisted of reaction tanks tightly coupled with measuring and recording devices. The research method used in the study enabled determining the activity of anaerobic sludge, susceptibility of the applied organic substrates to biodegradation, and quantity and composition of gaseous metabolites. The devices recorded and analyzed changes in the partial pressure inside the measuring tank evoked by biogas production in anaerobic processes run by microorganisms. In each of the experimental variants, 50 cm^3 of anaerobic sludge obtained from a municipal waste water treatment plant were administered to the measuring tank, followed by various doses of the substrate and various doses of chemical agent applied for the proper functioning of chemical toilets (e.g. on sailboats): Aqua Kem Green. The 100% dose was assumed to be the dose of bronopol containing chemical whose quantity recommended by the producer mixes at the ratio of 50/50 with feedstock for fermentation.

The complete measuring kit, made of a reaction tank and a measuring-recording device, was fixed in a thermostatic cabinet with hysteresis not exceeding ± 0.5 °C. Measurements were performed at 35 °C for 20 days, with the pressure in the reaction tank being measured every 15 min. Before the end of the measurement, 30% sodium base (NaOH) was introduced to a special container mounted inside the reaction tank, which enabled carbon dioxide to precipitate from the gaseous phase. A decrease of pressure in the reaction tank corresponded to the content of carbon dioxide, whereas otherwise the value of pressure depended on the content of methane. In respirometric analyses, calculations are based on the equation of ideal gas:

$$n = \frac{pV}{RT} \tag{1}$$

where: n – number of moles of gas, p – gas pressure [Pa], V – gas volume [m^3], R – universal gas constant (8.314 J/(mol·K)), T – temperature [K].

The content of carbon in the gaseous phase was calculated from the following equation:

$$n_{CO_2} + n_{CH_4} = \frac{p_1 V_g}{RT} \times 10^{-4} \tag{2}$$

where: n_{CO_2} + n_{CH_4} – number of produced moles of carbon dioxide and methane, p_1 – difference in gas pressure in a measuring tank at the beginning and at the end of the experiment caused by oxygen consumption and absorption of the generated CO_2 [hPa], V_g – volume of gaseous phase in a measuring tank [cm^3], R – gas constant, T – temperature of incubation [K], 10^{-4} – conversion factor.

The content of carbon dioxide in the gaseous phase was calculated from the following equation:

$$n_{CO_2} = \left(\frac{p_1 V_g - p_2 (V_g - V_{KOH})}{RT} \right) \times 10^{-4} \tag{3}$$

where: n_{CO_2} – number of produced moles of carbon dioxide [mol], p_2 – difference in gas pressure in an appropriate measuring tank at the end of the experiment minus pressure recorded at the beginning of the experiment minus pressure recorded in a blank sample after addition of KOH solution [hPa], V_{KOH} – volume of KOH solution [cm^3].

The content of methane in the gaseous phase was calculated from the following equation:

$$n_{CH_4} = n_{CO_2 + CH_4} - n_{CO_2} \tag{4}$$

Results of respirometric analyses allowed one to determine the rate of biogas production as affected by doses of the chemical agents Aqua Kem Green. Measurements of pressure inside the tank, made in 15 min intervals, enabled determining the rate of the process. Reaction rate constants were determined based on the experimental data by the method of non-linear regression using the Statistica 8.0 PL software. The iterative method was applied, in which in each iterative step a function is replaced with a linear differential relative to the determined parameters. The coefficient of concordance φ_2 was adopted as a measure of curve fitting (with the parameters determined in the study) to experimental data. This coefficient is a ratio of the sum of squared deviations of values calculated based on the determined function from experimental data, to the sum of squared deviations of experimental values from the mean value. Thus, the lower the value of the φ_2 coefficient, the better consistency is obtained. The fitting of the model to experimental points was adopted at the level at which the coefficient of concordance did not exceed 0.2.

3. RESULTS AND DISCUSSION

The applied 0.187 cm^3 dose of Aqua Kem Green chemical enabled producing 118 $m_N^3/T_{o.d.m.}$ of biogas at the constant for all samples loading of the measuring tank with a feedstock of organic compounds, i.e. 2.5 $kg_{o.d.m.}/m^3$. The total volume of biogas produced in this sample reached 295 cm^3, whereas methane content accounted for 59%. The rate of biogas production resulting from anaerobic metabolism reached 0.25 $m_N^3/(T_{o.d.m.} \cdot h)$. Increasing the dose of the bronopol containing chemical to 150% caused a negligible decrease in biogas production to 117 $m_N^3/T_{o.d.m.}$. The total quantity of biogas produced accounted for 294 cm^3 and methane content oscillated at the level of 58%. The rate of the reaction was observed to decrease slightly and reached 0.24 $m_N^3/(T_{o.d.m.} \cdot h)$. In turn, decreasing the dose of the chemical agent to 75% and 50% enhanced the production of biogas to the level of 124 $m_N^3/T_{o.d.m.}$. The total volume of sewage gas was 310 and 311 cm^3, with the reaction rate of ca. 0.26 $m_N^3/(T_{o.d.m.} \cdot h)$ and methane content at the level of 64% and 60%. Once Aqua Kem Green was applied at the dose of 25%, the efficiency of the process reached 129 $m_N^3/T_{o.d.m.}$, its rate accounted for 0.27 $m_N^3/(T_{o.d.m.} \cdot h)$, the total quantity of biogas produced for 322 cm^3 and methane content for 59%. In the blank sample with no bronopol containing chemical added, the production of biogas reached 127 $m_N^3/T_{o.d.m.}$, the total volume of biogas obtained reached 318 cm^3, and methane content remained at the level of 57%.

Application of the same dose of Aqua Kem Green chemical in another variant, at a constant loading of the measuring tank for all samples with the feedstock of organic compounds, i.e. 5.0 $kg_{o.d.m.}/m^3$ led to slightly higher efficiency of the process. The applied 0.187 cm^3 dose enabled producing 130 $m_N^3/T_{o.d.m.}$ of biogas. The total volume of biogas produced in this sample reached 325 cm^3, whereas methane content accounted for 60%. The rate of biogas production resulting from anaerobic metabolism reached 0.27 $m_N^3/(T_{o.d.m.} \cdot h)$. Increasing the dose of the bronopol containing chemical to 150% caused a negligible decrease in biogas production to 129 $m_N^3/T_{o.d.m.}$. The total quantity of biogas produced accounted for 323 cm^3 and methane content oscillated at the level of 60%. The rate of the reaction was 0.27 $m_N^3/(T_{o.d.m.} \cdot h)$. In turn, decreasing the dose of the chemical agent to 75% decreased the production of biogas to the level of 127 $m_N^3/T_{o.d.m.}$. The total volume of sewage gas was 317 cm^3, with the reaction rate of ca. 0.26 $m_N^3/(T_{o.d.m.} \cdot h)$ and methane content at the level of 63%. The dose of 50%

caused increase in biogas production to 130 $m_N^3/T_{o.d.m.}$. The total volume of sewage gas was 326 cm^3, with the reaction rate of ca. 0.27 $m_N^3/(T_{o.d.m.}\cdot h)$ and methane content at the level of 60%. Once Aqua Kem Green was applied at the dose of 25%, the efficiency of the process reached 131 $m_N^3/T_{o.d.m.}$, its rate accounted for 0.27 $m_N^3/(T_{o.d.m.}\cdot h)$, the total quantity of biogas produced– for 329 cm^3 and methane content – for 62%. In the blank sample with no bronopol containing chemical added, the production of biogas reached 136 $m_N^3/T_{o.d.m.}$, the total volume of biogas obtained reached 340 cm^3, and methane content remained at the level of 59%.

The volume of biogas produced, the content of methane and the rate of sewage gas production expressed per normal conditions (blank sample) obtained the experiment are presented in Tables 1, 2.

Table 1

Results of respirometric measurements with the use of various doses of Aqua Kem Green at loading of the measuring tank with a feedstock of organic compounds 2.5 $kg_{o.d.m.}/m^3$

No.	Dose of Aqua Kem Green	Biogas production		Methane content [%]	Rate $[m_N^3/(T\ o.d.m.\cdot h)]$
		$[m_N^3/T\ o.d.m.]$	$[cm_N^3]$		
1	150% (0.281cm^3)	117.60	294.0	58.0	0.24
2	100% (0.187cm^3)	118.12	295.3	59.0	0.25
3	75% (0.141cm^3)	123.90	309.7	59.4	0.26
4	50% (0.094cm^3)	124.60	311.5	61.2	0.26
5	25% (0.047cm^3)	128.62	321.6	59.3	0.27
6	–	127.05	317.6	57.3	0.26

Table 2

Results of respirometric measurements with the use of various doses of Aqua Kem Green at loading of the measuring tank with a feedstock of organic compounds 5 $kg_{o.d.m.}/m^3$

No.	Dose of Aqua Kem Green	Biogas production		Methane content [%]	Rate $[m_N^3/(T\ o.d.m.\cdot h)]$
		$[m_N^3/T\ o.d.m.]$	$[cm_N^3]$		
1	150% (0.281 cm^3)	129.32	323.3	60.0	0.27
2	100% (0.187 cm^3)	129.85	324.6	59.7	0.27
3	75% (0.141 cm^3)	126.87	317.2	63.7	0.26
4	50% (0.094 cm^3)	130.37	325.9	60.1	0.27
5	25% (0.047 cm^3)	131.42	328.6	62.3	0.27
6	–	135.97	339.9	59.2	0.28

Bronopol is a catalyst of oxidation of compounds containing thiol groups (SH) to disulfides [6]. This reaction is additionally characterized by a rapid oxygen consumption. In turn, one electron reduction of an oxygen molecule leads to generation of a strongly reactive superoxide anion. It oxidizes intracellular thiols, including glutathione. The latter is one of the most common low-molecular antioxidants. Oxidation results in the generation of glutathione disulfide. The reaction itself proceeds owing to a specific structure of a glutathione molecule, being a tripeptide containing cysteine, which, in turn, contains thiol groups (SH) susceptible to the action of superoxide anions. Oxidative stress results in disruption of the physical continuity of cellular structures and in disorders of biochemical transformations. Cell metabolism is thereby disturbed, which is manifested by inhibition of its growth and development [5, 6]. The results of examination show that such inhibition proceeds already at a 50% dose of Aqua Kem Green chemical at the first stage of experiment with anaerobic reactor load of feedstock reaching 2.5 $kg_{o.d.m.}/m^3$ as well as at the lowest dose of the chemical applied at the latter stage (tank load – 5 $kg_{o.d.m.}/m^3$). This is indicated by a decrease in the process rate and in the intensity of biogas production.

Free radicals (superoxide anions) might be neutralized owing to the action of catalase and superoxide dismutase (intracellular bacterial enzymes), according to the following reaction:

$$2H^+ + 2O_2^- \xrightarrow[\text{dismutase}]{\text{superoxide}} 2H_2O_2 \xrightarrow{\text{catalase}} 2H_2O + O_2$$

Yet, the rate of oxidation of thiols determined by bronopol concentration is also of significance in terms of the neutralization of bronopol. Once bronopol concentration is so high that the concentration of enzymes in a cell appears to be insufficient, the oxidative stress occurs.

The bactericidal effect of bronopol may be neutralized under anaerobic conditions, which has been proved by applying relatively low concentration of the bronopol containing agent at the first stage of the experiment. With its concentration reaching 25%, the volume of biogas produced was not reduced but even increased, which points to the enhanced activity of fermentation bacteria. Shepherd et al. [7] prove that another reaction may occur in which bronopol is consumed and neutralized. It does not require oxygen and is slower than oxidation of thiols where bronopol is only a catalyst. This reaction is determined by the concentration of thiols [7] and affords the possibility of neutralizing wastewaters containing bronopol in the course of methane fermentation.

4. CONCLUSIONS

Increasing concentration of Aqua Kem Green chemical leads only to minor inhibition of fermentation processes in anaerobic reactors, which results from effective neutralization of bronopol occurring in that chemical agent.

Introduction of a low dose of Aqua Kem Green chemical (25%) to anaerobic reactors (with the load of 2.5 $kg_{o.d.m.}/m^3$) does not affect the fermentation processes.

Increasing the load of the reactor with a feedstock of organic compounds from 2.5 to 5 $kg_{o.d.m.}/m^3$ has no significant effect on the effectiveness of biogas production.

Wastewaters produced on yachts and accumulated in chemical toilets with the described chemical agent may be dosed together with plant biomass to agricultural biogas works, without any significant disturbances in the biological processes run therein.

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