Original Research

Effect of Constant Magnetic Field (CMF) with Various Values of Magnetic Induction on Effectiveness of Dairy Wastewater Treatment under Anaerobic Conditions

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Abstract

This study was undertaken in order to determine the effects of the constant magnetic field (CMF) on the effectiveness of dairy wastewater treatment under anaerobic conditions. It demonstrated that increasing the value of the magnetic flux in the analyzed range resulted in an increasing effectiveness of the fermentation process. Magnets with induction of 0.38 [T] elicited significant changes in the analyzed parameters of methane fermentation. The magnetic field (MF) was observed to positively affect the sedimentation process of anaerobic sludge, reduced COD concentration in the effluent, and biogas production rate. In the most effective variant, the content of suspended matter in the treated wastewaters was reduced by 26.1% and the effectiveness of COD removal increased by 14.0%, compared to the variant without the application of the physical factor. Magnetic induction of 0.431 caused significant changes in the analyzed parameters of the methane fermentation process.

Keywords: wastewater treatment, anaerobic conditions, dairy wastewater, whey, constant magnetic field, methane fermentation, biogas

Introduction

The method of magnetic treatment of a fluid has so far been implemented mostly in systems where scale formation was observed, mainly due to the flow of a factor, heating and exchange of heat, and where the network and tanks were subject to internal corrosion. It has been demonstrated that exposure of aqueous salt solutions to the effect of a magnetic field (MF) causes crystallization of calcium forms into aragonite and vaterite. Both forms do not cause scale deposition on walls of the installation but in the entire vol-

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ume of water, and the suspension being formed is devoid of cementing properties [1-3].

It seems, however, that methods of magnetic treatment of fluids may be exploited in a significantly wider scale, because with appropriately selected parameters the process exerts a positive effect on many other properties of a fluid, including wastewaters and anaerobic sludges. Changes in properties of solutions being directly exposed to the effect of the constant magnetic field (CMF) are linked, among other things, with modification of their molecular structure, polarization and ordering of particles as well as with a change in the electric charge [4]. At the site of direct exposure to the CMF there occurs selective ionization, circulat-

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Series	Diameter ±0.1 [mm]	flux ×		Magnet. Moment ×10-6 [mWb×m]	Magnet. induction in geo- metric center of the surface of magnetic pole at the dis- tance of 0.7 mm [T]	Magnet. induction near the edge of the surface of magnetic pole at the dis- tance of 0.7 mm [T]	Lifting capacity [kg]
1	lack of constant magnetic field						
2	5	1	~173	~19.722	~0.160	~0.170	~0.2
3	5	5	~1,005	~114.57	~0.388	~0.391	~0.85
4	5	10	~2,036	~232.104	~0.422	~0.432	~0.95
5	5	15	~3,016	~343.824	~0.431	~0.454	~1.1

Table 1. Experimental series and technical parameters of the constant magnets used in the study.

ing rotary currents are being formed, inner electric and magnetic fields are being generated, changes occur in electrical conductance of solutions, and additional magnetic moments are appearing. Molecules are polarized, ordered, and receive an appropriate charge.

Investigations conducted so far and addressing the impact of the MF on changes in fluid properties have demonstrated the possibility of modifying the pH value of the medium being treated. Both the tap and distilled water displayed multi-extreme changes in pH value. This fact has been confirmed by many researchers [1, 3-5] and the phenomenon has been found to apply also to municipal wastewaters [6, 7].

Studies also have corroborated the efficiency of applying the CMF on the biological and enzymatic activity of microorganisms responsible for wastewater treatment processes [3]. Aarthi et al. demonstrated that pre-treatment of Flavobacterium species with sinusoidal MF appears to result in a more effective degradation of paper mill effluents. Flavobacterium species were found to have four times with respect to growth when exposed to CMF of 10 HZ, 100 Nt for 30 h, and simultaneously, the BOD, COD, lignin, phenol and protein content were reduced in the effluent using CMF-treated cells [8].

Xu and Sun determined the impact of the CMF on the removal of Cr (VI) in the SBR system. They evaluated the effect of MF on the growth and proliferation of predominating bacterial strains and their capability to remove Cr (VI). Duration of the reaction until the moment of chromium removal turned out to be significantly shorter in the presence of MF (by 2 hours on average). This experiment confirmed also that the MF may improve sedimentation capability of activated sludge, reduce the concentration of suspensions in the effluent, and increase the effectiveness of wastewater treatment [9].

Sparse works are available on the feasibility of applying the MF in anaerobic processes of wastewater treatment. Hence, there is an actual need to undertake research that will enable determining the impact of this physical factor on the achieved technological effects linked with reduced concentrations of contaminants and with the quantity and qualitative composition of biogas produced. Properties of the CMF described in literature may facilitate sedimentation of the anaerobic sludge [10, 11]. In view of the above,

the objective of this study was to determine the effect of the CMF generated using neodymium magnets on the effectiveness of diary wastewater treatment in the process of methane fermentation.

Experimental Procedures

Our study was carried out under laboratory conditions using kits for respirometric measurements of anaerobic processes by the TWT company. It was divided into five experimental series, with the criterion being the value of magnetic induction applied (Table 1).

The experiments were conducted under conditions of mesophilic fermentation at 35°C. Measuring kits were fixed in a shaker with a water bath, keeping the assumed temperature exact to ± 1.0 °C. Wastewater retention time in the experimental system reached 5 days. The initial loading of model fermentation tanks with a feedstock of organic compounds characterized by the COD value accounted for 10 g COD/dm³.

The CMF was generated by sintered permanent neodymium magnets of rare-earth – metal type ($Nd_2Fe_{14}B$). The magnetic and physical properties of the magnets applied in the study were presented below:

- induction of residual flux density (remanence) B_r 1.21-1.25 [T]
- coercive force H_{cB} min. 899 [kA/m]
- coercive force H_{cJ} min. 955 [kA/m]
- density of magnetic energy (BH)_{max} 286-302 [kJ/m³]
- density $\sim 7.5 \, [\text{kg/dm}^3]$
- Vickers' hardness (HV) ~600 [kG/mm²]
- resistivity ~144 [uOhm×cm]

The maximum temperature of work of the applied permanent magnets accounted for \leq 80°C, Curie temperature for \sim 310°C, temperature coefficient of remanence TK(B_r) for \sim -0.12%/°C, and temperature coefficient of coercivity TK(H_{cl}) for \sim -0.6%/°C. Magnetizing direction: alongside height, which means that one circular surface of the magnet constitutes the N pole, whereas the other, opposite circular surface of the magnet constitutes the S pole. Technical parameters of the applied magnets are presented in Table 1.

Table 2. Preparation of experimental kits for respirometric measurements.

	Loading of a measuring tank with COD feedstock	Sludge volume	Weighted portion of milk powder	Sludge loading with COD feedstock	
10.0 g/dm³		200 cm ³	2.0 g	2.05 g/g _{d.m.}	

Table 3. Values of contamination indicators in the dissolved phase of supernatant immediately after the addition of the weighted portion of milk powder.

Indicator	Unit	Mean	Standard dev.
COD	$[mgO_2/dm^3]$	11,250.3	320.9
BOD ₅	[mgO ₂ /dm ³]	8,010.5	294.2
N _{tot.}	[mg N/dm³]	439.8	41.5
P _{tot.}	[mg P/dm³]	82.7	17.1
рН	-	7.11	0.28

Table 4. Characteristics of anaerobic sludge used in the experiment.

Parameter	Unit	Min. value	Max. value	Mean	Standard deviation
pH	-	7.89	8.08	7.98	0.10
Hydration	[%]	96.40	97.10	96.75	0.49
Dry matter	[%]	2.90	3.60	3.25	0.31
Volatile substances	[% d.m.]	47.32	51.04	49.18	2.63
Ash	[% d.m.]	48.96	52.68	50.82	1.86
CST	[s]	466	479	472.5	9.2
COD of eluate	[mgO ₂ /dm³]	736	752.8	744.4	11.9
TOC of eluate	[mg/dm³]	413.95	681.45	547.7	189.15

Experiments were conducted with the use of model dairy wastewaters prepared from skimmed milk powder. To each reaction tank 200 cm³ of anaerobic sludge were introduced, then a weighted portion (0.2 g) of milk powder was added to the tanks and dissolved in a solution of the anaerobic activated sludge. Experimental parameters were presented in Table 2, whereas values of major contaminants in the dissolved phase of the supernatant after the addition of the weighted portion of milk powder were collated in Table 3.

For inoculation of the respirometric reactors use was made of the anaerobic activated sludge originating from a closed fermentation tank of a municipal wastewater treatment plant. The characteristics of the activated sludge used in the experiment was provided in Table 4.

Depending on the experimental series, an appropriate neodymium magnet was fixed inside the reaction tank (Table 1). Using a nylon cord, the magnet was fixed at half the height of the layer of a mixture of anaerobic sludge and model dairy wastewaters. Afterward, the samples were purged with nitrogen until anaerobic conditions had been reached in the reaction tank. The measuring kits were placed in an *Elpin* type 357 water bath with shaking. The

reaction tank was close-coupled with a measuring-recording device that measured and recorded changes in the partial pressure inside the reaction tank. Anaerobic decomposition of organic compounds contained in the model dairy wastewaters led to the generation of sewage gas (mainly of: CH₄ and CO₂). This in turn elicited a pressure increase in the reaction tank. The changes of pressure were measured and registered by the controlling-measuring device with a frequency of 15 min.

Calculations made in respirometric analysis are based on the equation of perfect gas. The measured value of pressure change inside the measuring tank enables computing the number of moles and volume of produced biogas expressed per normal conditions:

$$n_{CH_4/CO_2} = \frac{\Delta p \times V_g}{R \times T} \times 10^{-4}$$

...where:

 n – number of produced moles of biogas containing methane and dioxide (excluding trace amounts of hydrogen sulfide and hydrogen) [mol] 258 Zieliński M., et al.

 Δp — difference in the pressure of gas inside the measuring vessel at the beginning of the experiment and before the addition of sodium base, caused by biogas production [Pa]

V - volume of gaseous phase in a measuring tank [m³]

R – gas constant [8.314 J/mol·K]

T – temperature of incubation [K]

10⁴ - conversion factor ([Pa] into [hPa] and [m³] into [cm³])

At the end of the respirometric measurement, analysis was conducted for the composition of biogas produced. To this end, samples of biogas were collected from measuring vessels with the use of a needle and a gas-tight syringe. Measuring vessels were equipped in snorkels with rubber stoppers enabling gas-tight collection of samples. A single sample included 20 ml of biogas. The composition of biogas and the percentage content of its major components were analyzed with a gas chromatograph GC *Agillent 7890* A, equipped in a thermoconductometric detector (TCD).

After a 5-day reaction, the quality of treated waste-waters was analyzed in a measuring flask. To this end, mixing was switched off and the sludge was left for sedimentation. After 1.5-h sedimentation, the supernatant was collected from the measuring vessel. In all experimental series, the supernatant was collected at a depth of 1.0 cm below the fluid table. The collected sample was analyzed for the concentration of suspensions and contents of organic compounds characterized by the COD value. Respirometric analysis were conducted in triplicate.

Statistical analysis of the obtained results was done using variance analysis, at the assumpted accuracy level (p < 0.05). Normal distribution was confirmed by Szapiro-Wilk test, and hypothesis concerning variance homogeneity inside the groups were verified on the basis of Leveney's test. Analysis of the differences between means from the particular groups was done using Tukey's test.

Results and Discussion

Based on the analyses conducted in the experiment it was established that the application of magnetic activation of the methane fermentation processes affected positively the technological effects of organic compound removal as well as the production and composition of biogas.

The content of organic compounds in the supernatant was determined as the content of COD. In respect of the control series where COD content reached 4,050 mgO₂/dm³, the lowest concentration of organic compounds was reported in series 5, i.e. 3,474 mgO₂/dm³ on average. In this case, the effectiveness of organic compounds removal increased by 14% (Fig. 1).

Investigations on the effect of a physical factor on COD reduction from crude wastewaters were carried out by Tomska and Wolny [12]. They demonstrated that the MF with induction of 40 mT did not contribute to enhanced reduction of COD from crude wastewaters and had a positive effect only on the nitrogen compounds. The magnetizer was placed on a pipe used for recirculation of activated

sludge. In that case, the crude wastewaters treated were domestic sewage. No significant differences were noted in the effectiveness of organic contaminant biodegradation between the system with MF and the control one.

Yavuz and Celebi [7] were investigating the effect of MF on the activity of activated sludge in the process of wastewater treatment. Analyses were carried out at varying pH values of wastewaters (in the range of pH 6.0÷8.5), and at varying induction of the MF (in the range of 8.9÷46.6 mT). In the variant with the MF applied, the effectiveness of the treatment process was higher by 44% than in the control variant. The maximum activity of microorganisms was noted at magnetic induction of 17.8 mT, whereas along with an increasing MF induction value it was observed to diminish. Those authors demonstrated that the MF exerted a positive effect on the metabolic activity of microorganisms, which contributed to enhanced effectiveness and, therefor, to the improved effects of the wastewater treatment process. This also was the case in the reported experiment. The physical factor was observed to elicit a positive effect on the activity of activated sludge microorganisms, which has been corroborated by the achieved effects of the treatment process in respect to control.

Ji et al. studied the effect of MF on the activity of activated sludge wastewater treatment process. Wastewater used in the study was characterized by the presence of organic compounds similar to the composition of municipal sewage. Analyses were carried out at different pH values (3-12), the induction of different MF (0-500 mT), different times of the process (0-60 h), and at different temperatures (10-50°C). The highest activity of microorganisms found in the magnetic induction of 5.0 and 20.0 mT, which beneficially affect the mixed culture of bacteria in activated sludge (especially in the elongation of the stationary phase of growth). Increasing magnetic induction caused the opposite effect. Degradation of organic compounds was observed at the level of 37-40%. Optimal biodegradation conditions set out in the study conducted by the authors of the biodegradation time 48h, magnetic induction field of 20.0 mT, the temperature in the range of 20-40°C, and pH between 6 and 10 [13].

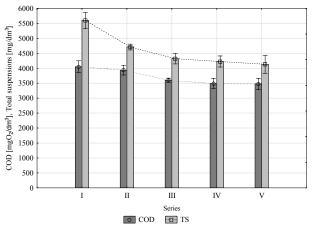


Fig. 1. Content of total suspensions and COD values in outflow from reactors in successive experimental series.

Owing to the application of the CMF the concentration of dry matter of the sludge in the supernatant collected from model fermentation tanks was significantly lower than in the control series. In the case of series 2, the content of suspended matter in the supernatant decreased by 16% compared to the control tank, whereas the increased flux of MF in series 3 caused the concentration of suspended matter to diminish by 23%. In the respirometric reactors with the CMF applied, the biomass of methane fermentation microorganisms was observed to sediment and thicken more efficiently. The lowest content of outflow total suspensions, i.e. 4,120 mg_{d,m}/dm³ on average, was determined in series 5, followed by the value of 4,225 mg_{d,m}/dm³ noted in series 4. The content of suspended matter in treated wastewaters from series 5 was lower by 26% (Fig. 1).

In turn, Hattori et al. [10] were examining the effect of an external MF on the sedimentation process of three types of activated sludge. The induction of the applied external MF was 80.0 and 500.0 mT. They demonstrated that the application of the physical factor affected improvement of the sedimentation processes irrespective of the properties of activated sludge. Simultaneously, they observed enhanced growth of the activated sludge exposed to the external MF.

In contrast, the reported experiment demonstrated that the activated sludge was occupying a lesser volume in the experimental reactor exposed to the effect of the physical factor than in the control reactor. Furthermore, Hattori et al. [9] established that the addition of FeCl₃ intensified the effect of the physical factor. Based on results achieved, they postulated using an external MF as a factor improving sedimentation process of the activated sludge. Ying et al., to enhance the impact of treatment of wastewater from the milking parlor, applied Fe₃O₄ added to the sediment. This results in high efficiency of removing 94% organic compounds and improved sludge thickening and separating it from the liquid [11].

The study on the effect of magnetic treatment on changes in physicochemical properties of municipal sewage proved that the period necessary for complete sedimentation in magnetized sewage shortened significantly compared to respective period noted in the system without magnetic activation. What is more, studies confirmed the tendency for coagulation of small particles of sludge in magnetically-prepared wastewaters, which affected the acceleration of their sedimentation and increased their dehydratability [6, 11].

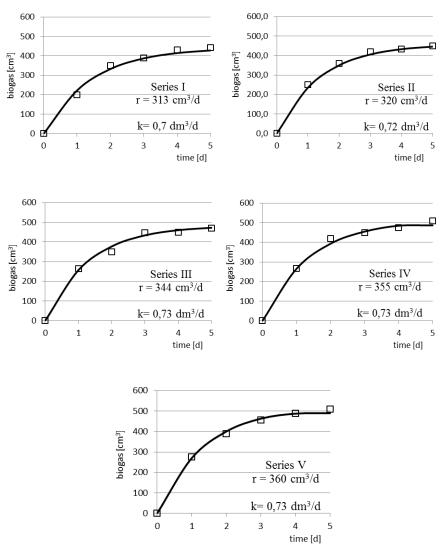


Fig. 2. Curves of biogas production rate in the successive experimental series.

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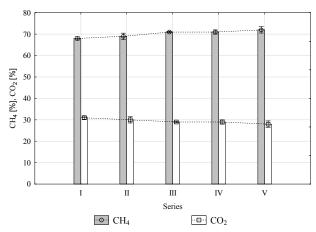


Fig. 3. Percentage content of major components of biogas in the successive experimental series.

In the experimental series with the application of the CMF, the maximum mean value of biogas production coefficient reaching 367 [cm³/g_{rem.COD}] was noted in series 5, whereas in the control series the corresponding value accounted for 350 [cm³/g_{rem.COD}]. This means an increase in the quantity of biogas produced under measuring conditions by ca. 4.6%, on average. The greatest increase in the value of this coefficient occurred in series 3, at a nearly sixfold increase in the size of magnetic flux of the permanent magnet introduced to the measuring tank. In this case, the mean value of biogas production coefficient increased from 353 [cm³/g_{rem.COD}] in series 2 to 361 [cm³/g_{rem.COD}] in series 3. The successive increase in the value of the magnetic flux in the subsequent experimental series did not cause any significant increase in biogas production (Fig. 2).

It also has been proved that strong magnetic fields with appropriately selected parameters affected changes in such properties of a fluid as: surface tension, density, viscosity, light extinction, and wettability of solid bodies [3, 5]. This may appear significant from the viewpoint of both more effective sedimentation of the sludge in reactors as well as removal of gaseous metabolites of anaerobes.

The reaction of anaerobic degradation of model dairy wastewaters proceeded according to the first order reaction in all experimental series. Results achieved in this respect were presented in Fig. 2. In the control series the rate of biogas production reached 313 cm³/d, whereas in series 2 it increased barely to 320 cm³/d. The greatest increase in biogas production rate occurred between series 2 and 3. The increase of magnetic induction of the applied magnet from 0.16 T to 0.39 T caused an increase in methane fermentation rate from 320 cm³/d to 344 cm³/d. A successive increase in the magnetic flux of the applied magnets in the subsequent experimental series did not evoke any significant increase in reaction rate. The maximum value, accounting for 360 cm³/d, was achieved in series 5 (Fig. 2).

The analysis of biogas composition demonstrated that there were no significant differences between the experimental series. In series 1, without the magnetic field, the mean content of methane was at a level of 68%. In series 2, after the application of a magnet with the magnetic flux of

 $1,005\times10^3$ [mWb], the mean content of methane accounted for 69% (Fig. 2). In turn, at the highest value of the magnetic flux, i.e. $3,016\times10^3$ [mWb] in series 5, the mean concentration of methane in biogas produced reached 72%, which indicates a 4% increase compared to the control series (Fig. 3).

Conclusions

Under experimental conditions applied, the CMF was shown to exert a significant effect on the process of methane fermentation. An increase was observed in the value of biogas production coefficient and in the rate of biogas production along with an increasing value of magnetic induction. But still, positive effects were achieved at the lowest value of the magnetic flux, i.e. 173×10^3 [mWb]. The magnets with induction of 0.38 [T] caused significant changes in the analyzed parameters of the methane fermentation process. The increasing magnetic induction had no significant effect on reaching higher final effects. The analysis of biogas composition demonstrated that there were no significant differences between particular experimental series.

A positive effect of the MF was established in respect to the sedimentation process of anaerobic sludge and reduction of COD concentration in the effluent. In the most effective variant, at the magnetic flux of 3,016×10⁻³ [mWb], the content of suspended matter in the treated wastewaters was lower by 26.1%, and the effectiveness of COD removal increased by 14.0% compared to the variant without the physical factor. Minimization of biomass elution from anaerobic reactors is of key significance to their effective work. Ample modernization and developmental actions undertaken in this area are focused on attenuating the negative process of biomass escape. One of the feasible solutions is the application of CMF.

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