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POSSIBILITY OF IMPROVING TECHNOLOGICAL EFFECTIVENESS OF DAIRY WASTEWATER TREATMENT THROUGH APPLICATION OF ACTIVE FILLINGS AND MICROWAVE RADIATION

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The aim of the study was to determine the technological effectiveness of treatment process of model dairy wastewater in anaerobic reactors with active filling (AF), heated with electromagnetic microwave radiation (EMR). Experiments were conducted in a laboratory scale. The AF were produced using micro-pore extrusion technology. The study demonstrated that AF introduction to the technological system and application of EMR significantly improved the effectiveness of organic compounds, phosphorus removal and biogas production. Initial organic loading rate also affected the final results of wastewater treatment.

Keywords: microwave radiation, active filling, fermentation, dairy wastewaters, wastewaters treatment.

Introduction

Popularity of anaerobic digestion in wastewater treatment processes stems from technological benefits gained, low exploitation costs and possibility of energy recovery [1 – 3]. The main drawback of solutions based on the anaerobic process is the low effectiveness of nitrogen and phosphorus removal involving only the coverage of the demand for these elements by fermentation bacteria [4]. This phenomenon necessitates the use of additional technological processes including chemical precipitation of phosphorus or the use of aerobic treatment. Although effective, these methods generate additional exploitation costs and require assuring specific technological parameters [5, 6]. An alternative to currently applied solutions is the use of fillings that aid the processes of sorption, precipitation and binding of biogenic compounds [7, 8]. Effective removal of phosphorus under anaerobic conditions has been proved feasible

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upon the introduction of metal ions formed as a result of metal elements corrosion [9, 10]. Laboratory-scale research proves that the use of metals dissolution method enables complete removal of orthophosphates and 90% reduction of organic phosphorus concentration [11].

A significant physical parameter influencing the effectiveness of methane fermentation processes is temperature stimulated by conductivity, convection or microwave radiation [12 – 14]. Our previous investigations showed that the electromagnetic microwave radiation elicited not only an increase in kinetic energy in the system but additionally catalyzedthe biochemical activity of fermentation microflora induced by the so-called athermal effect [15, 16]. The athermal effect of sludge microwaves triggers changes at a molecular and taxonomic level [17 – 20].

The aim of this study was to determine the technological effectiveness of treatment process of model dairy wastewater in anaerobic reactors with active filling (AF), heated with electromagnetic microwave radiation (EMR).

Experimental

Experiments were conducted in a laboratory scale with the use of anaerobic reactors with an active volume of 1.0 dm^3, that were convective heated and microwave heated. The process was run at a temperature of 35°C and the hydraulic retention time (HRT) reached 120 h. The EMR was generated with magnetrons by "Plazmotronika Company", with the power of 800 W. The EMR was transmitted to the technological system with wave-guides. The frequency of EMR was 2.45 GHz. Contents of the reactors were mixed with magnetic stirrers IKA RW 16 basic.

The study analyzed also the impact of applying AF on the anaerobic digestion of dairy wastewater. The spherical filling was manufactured by microporous extrusion of granulated transparent and plasticised polyvinyl chloride (PVC). PVC, commercially available as Alfavinyl GFM/4–31–TR, was manufactured by Alfa Sp. z o.o. (Poland). Major parameters of the PVC used in the experiment are as follows: density 1230 kg/m^3, Young’s modulus 2600 MPa, tensile strength 21 MPa, elongation at break 300%, shore A-hardness 80°Sh. Additionally, the AF contained different proportions of Fe and Cu powders by "Cometox". Each time, the quantity of introduced metals reached 5.0% by weights.

The AF were produced using the micro-pore extrusion technology. The proposed solution is an innovative technology that has so far never been used to produce elements that would constitute a medium for the growth of microflora responsible for degradation of contaminants. The micro-pore extrusion of poly(vinyl chloride) was conducted using a porophore in the form of a granulate with the commercial name Hydrocerol 530, produced by "Clariant Masterbatch". The process was run with a mixture containing 50% of a blowing agent and a nucleodizing agent. The initial temperature of Hydrocerol 530 was 170°C. The physical parameters of AF applied in the study were as follow: density 892.7 kg/m^3, porosity 39.66%, hardness 23.9°Sh, tensile strength 138.97 MPa.

At the beginning of experiments, the reactors were fed with 200.0 cm^3 of anaerobic sludge originating from a closed fermentation tank of a municipal wastewater treatment plant in Olsztyn and with 100.0 g of AF. The concentration of volatile solids (VS) seeded into the reactor was 68.46±2.53% of the total solids (TS). Next, the assumed doses of model dairy wastewaters, produced based on milk powder, were introduced to the reaction mixture. In order to remove oxygen, the whole reactor's content was blown through with N_2 for 5 min. Particular experimental variants differed in the initial chemical oxygen demand (COD) concentration in dairy wastewater. The characteristics of dairy wastewater were as follow: 5-day biochemical oxygen demand (BOD_5) 5605.11±178.11 mg O_2/dm^3, COD 10009.13±723.13 mg O/dm^3, BOD_5/COD 0.57±0.01, pH 7.43±0.14, suspended matter 519.40±29.90 mg/dm^3, total nitrogen (TN) 363.47±35.30 mg N/dm^3, ammonia nitrogen (AN) 48.52±6.86 mg N-NH_4/dm^3, total phosphorus (TP) 297.05±35.71 mg P/dm^3, orthophosphate 19.83±1.98 mg P-PO_4/dm^3.

The experiment was divided according to the method of heating (stages), type of AF tested (series) and initial COD concentration in dairy wastewater. Design of the experiment was presented in Table 1.

Table 1. Experimental design

Substance, %	Stage									
	Convective heating					Microwave heating				
	Series									
	I	II	III	IV	V	I	II	III	IV	V
Cu	0	5	10	15	20	0	5	10	15	20
Fe	0	95	90	85	80	0	95	90	85	80
Variant	(1) 2.0 g COD/dm^3					(1) 2.0 g COD/dm^3				
	(2) 4.0 g COD/dm^3					(2) 4.0 g COD/dm^3				
	(3) 6.0 g COD/dm^3					(3) 6.0 g COD/dm^3				
	(4) 8.0 g COD/dm^3					(4) 8.0 g COD/dm^3				

Temperature in the reactors and changes in the pressure of biogas produced were monitored continuously throughout the experiment with the use of an

840099 Sper Scientific manometer. The volume of biogas produced was computed based on the Clapeyron equation, whereas its qualitative composition was analyzed with a GC Agillent 7890 A gas chromatograph equipped in a thermoconductometric detector (TCD). Furthermore, basic indicators of contaminants, including COD, TN, TP and concentrations of Cu and Fe were controlled in wastewaters throughout the experiment with the use of a UV-Vis HACH Lange DR5000 spectrophotometer. The pH value of wastewaters was measured as well. Results achieved were analyzed statistically using a STATISTICA 10.0 PL package. The hypothesis on the distribution of each analyzed variable was verified with the Shapiro – Wilk W test. The significance of differences between variables was stated with the use of one-way analysis of variance (ANOVA). The homogeneity of variance in groups was checked with the Levene test. The significance of differences between analyzed variables was determined with the RIR Tukey test. Differences were found significant at $\alpha = 0.05$.

Results and discussion

The study demonstrated that the introduction of AF to anaerobic reactors and the use of EMR enhanced the contaminants removal, especially COD and phosphorus removal, and improved biogas production. The key impact on the final outcomes achieved was ascribed to the initial COD concentration in dairy wastewater.

The significant effect of applying AF on the COD removal was observed at COD ranging from 6.0 g COD/dm^3 to 8.0 COD/dm^3 (variants 3 – 4). In series I, the content of COD in the effluent reached 2959.6 mgO/dm^3 (series I, variant 4) (Fig. 1). The use of AF in series IV caused a reduction of the COD value to 1211.8 mgO/dm^3. A significant effect of EMR on COD value was observed only in the series where no AF was introduced to the anaerobic reactors. In that case, in variant 3, the COD value accounted for 2011.1 mgO/dm^3 in the convective-heated system and for 1463.7 mgO/dm^3 in the system with EMR, whereas in variant 4 the respective values reached 2959.6 and 2383.3 mgO/dm^3 (see Fig. 1).

The lowest efficiency of biogas production was observed in series I, with the efficiency decreasing from 374.9 cm^3/gCOD$_{rem}$ to 214.3 cm^3/gCOD$_{rem}$ along with COD loading increase. The application of AF provided higher effects at the analyzed range of COD from 4.0 g COD/dm^3 to 6.0 g COD/dm^3 (Table 2). The type of AF applied was found not to affect the efficiency of biogas production. In contrast, a significant effect of EMR was noted in the case of high COD from 4.0 g COD/dm^3 to 8.0 g COD/dm^3 in series II. For these two variants, the efficiency of biogas production ranged from 14.0 to 24.0%, compared to the reactors with convective heating (see Table 2). The concentration of methane in biogas produced fitted within the range of 43.2 to 67.4% depending on the experimental variant. The highest concentration of CH_4, reaching over 60.0%, was achieved at COD of 2.0 g COD/dm^3 and 4.0 g COD/dm^3. The impact of AF on methane content in biogas was noted in variants with COD from 6.0 to 8.0 g COD/dm^3. The concentration of methane in biogas was higher in variant 3 by 6.0% on average, whereas in variant 4 by nearly 9.0%. The application of EMR had no significant effect on biogas composition (see Table 2).

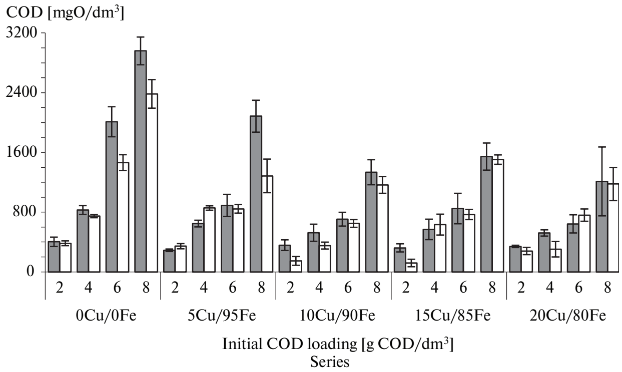

Fig. 1. COD concentrations in the effluent.

In the experiment, no significant effect of the applied technological solutions was found in respect of the efficiency of nitrogen compounds removal (Fig. 2). Irrespective of the composition of the analyzed AF and heating system applied, a similar efficiency of nitrogen removal was observed in the study. Nitrogen concentration in the effluent was increasing proportionally to COD increase from 2.0 to 8.0 kg COD/m^3 and fitted within the range of 131.2 – 237.5 mg TN/dm^3 (see Fig. 2). The effectiveness of TP removal exceeded 90%, irrespective of the AF used. In series I, the efficiency of TP removal did not exceed 10.0%. The EMR had no effect on the TP removal (Fig. 3).

Stable pH values around pH 7 were observed for initial COD ranging from 2.0 to 6.0 kg COD/m^3. Increasing the initial COD to 8.0 kg COD/m^3 caused a decrease in the pH value, but it was still higher than pH 6. The application of different AF in the subsequent experimental series had no direct impact on pH values. In the microwave-heated system the pH values were negligibly higher (pH 0.2 – 0.9) than in the system with convective heating.

The study demonstrated that along with an increasing ratio of copper to iron in the AF, higher concentrations of this metal were noted in the effluent.

Table 2. Biogas production and methane content in biogas from anaerobic digestion of dairy wastewater (mean ± std. dev.)

Parameter	Wariant	Stage									
		Convective heating					Microwaveheating				
		Series									
		I	II	III	IV	V	I	II	III	IV	V
Biogas [$cm^3/g\ COD_{rem}$]	(1) 2.0 g COD/dm^3	375±22	383±9	374±24	359±17	370±21	331±16	362±13	371±26	360±28	372±33
	(2) 4.0 g COD/dm^3	321±37	374±17	372±14	351±39	319±9	321±25	353±8	378±28	346±14	350±18
	(3) 6.0 g COD/dm^3	282±21	307±29	301±21	323±27	276±6	267±14	380±17	344±16	328±11	295±13
	(4) 8.0 g COD/dm^3	219±18	261±12	243±33	250±10	224±24	259±23	297±19	318±29	282±8	269±16
CH_4 , %	(1) 2.0 g COD/dm^3	64±4	62±5	65±1	66±1	65±2	66±2	63±2	64±3	64±1	63±2
	(2) 4.0 g COD/dm^3	66±6	62±4	64±2	64±1	63±3	66±3	61±2	63±2	64±1	64±1
	(3) 6.0 g COD/dm^3	56±2	54±6	62±3	57±3	54±4	54±5	60±4	61±2	61±3	53±2
	(4) 8.0 g COD/dm^3	44±6	48±3	53±5	53±3	49±5	48±2	51±6	51±4	58±2	52±3

The Cu concentration ranged from 0.0 mg Cu/dm^3 in series I to 0.07 mg Cu/dm^3 in series V. In turn, the concentration of iron in the effluent reached 0.24 mg Fe/dm^3 in series I to 3.5 mg Fe/dm^3 in series V.

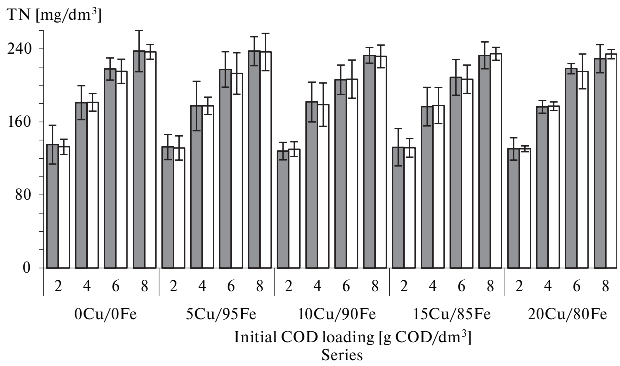

Fig. 2. TN concentrations in the effluent.

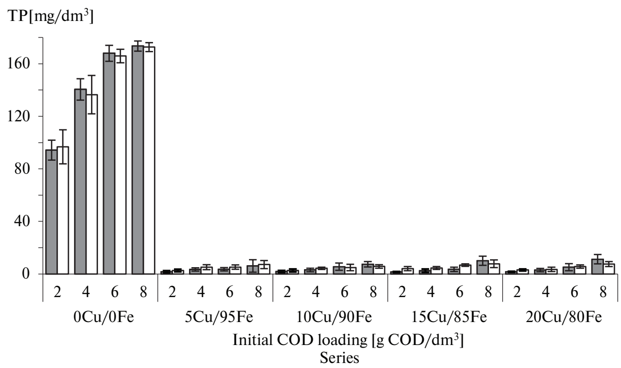

Fig. 3. TP concentrations in the effluent.

The solution described in this manuscript is an attempt of the innovative application of AF and EMR in wastewater treatment, but the results were diametrically different than those reported in the literature.

The rate of enzymatic reactions was found to depend on the presence and availability of components and enzyme activators. Copper ions (Cu^{2+}), occurring in active centers of the so-called metalloenzymes, are components of enzymatic reactions and, simultaneously, activators. However, when their concentration in the medium exceeds the permissible level, they may exert toxic effects on microorganisms, thus leading to inactivation of enzymes or nucleic acids [21, 22]. The phenomenon of treatment process inhibition was not observed in this study, which was indicated by an increased effectiveness of COD removal in the reactors with AF. This was, probably, due to a low concentration of copper determined in wastewaters. In addition, the study showed no significant effect of EMR on the removal of organic compounds. This phenomenon has also been confirmed in our previous studies [18, 20].

The effectiveness of biogas production and the concentration of methane in biogas were decreasing proportionally to an increasing of initial COD, irrespective of AF composition. The use of EMR positively affected the biogas/methane production. Similar conclusions were reached by Zielińska M. et al. [17]. who noted a decrease in biogas production at an increasing organic loading rate. They also observed an increase in biogas volume and percentage content of methane (ca. 67%) in the reactors exposed to EMR.

Another factor found to improve biogas quality was the reaction of iron ions (Fe^{2+}) with undesirable metabolites of anaerobic bacteria. This reaction resulted in the removal of H_2S and CO_2 from biogas, which affected an increase in methane concentration. The beneficial effect of iron on the enrichment and purification of biogas was confirmed by Lee H. and Shoda M. [23], where 6 – 8 g addition of iron caused methane concentration increase to 60%. Keeping the pH value at pH 7.5 caused precipitation of iron carbonate and iron sulfides, followed by their accumulation in the sludge, which finally resulted in a low concentration of H_2S and CO_2 in biogas [23]. In a research on the effect of steel fillings on the effectiveness of wastewater treatment, Wysocka I. and Krzemieniewski M. [11] achieved 90% effectiveness of sulfides removal from wastewaters, that were subsequently accumulated in the sludge.

The reported study demonstrated that the introduction of iron and copper to a filling structure did not cause any drastic increase in their concentrations in the effluents. Pathak A. et al. [24]. reported that copper content may vary between 112 and 2300 mg Cu/kg d.s.s. (dry sludge solids) depending on the type of sewage sludge. Furthermore, in a two-year cycle of investigations on the content of heavy metals in municipal sewage sludge, Ščančar J. et al. [25]. achieved the mean content of copper at 426 mg Cu/kg d.s.s. and that of iron at 22445 mg Fe/kg d.s.s.

In the current study, no effect of coupled application of AF and EMR was found on the removal of nitrogen compounds from dairy wastewaters. In contrast, a high effectiveness of phosphorus removal owing to chemical precipitation of its compounds with the excess of iron ions was noted. The high effectiveness of phosphorus compounds removal (97%) in rotating reactors filled with an iron ore was confirmed by Guo C. et al. [26]. In the experiment described by these authors, the filling with particle size of 7.6 mm enabled removing 25 mg P/dm$^3 \cdot$ d. The highest effectiveness of phosphorus removal was also confirmed by Tran N. et al. [27]. who, by using the electrocoagulation process, achieved the effectiveness of 96% .

Conclusion

Results presented in this manuscript confirmed that the combination of chemical and physical factors, i.e. introduction of a filling with admixture of iron and copper to the reactor and microwave heating of the substrate, may yield positive effects on the efficiency of dairy wastewater treatment.

The impact of applying AF on the high efficiency of COD removal was noted at initial COD between 6.0 and 8.0 COD/dm^3. In turn, a significant effect of EMR on the COD removal was observed only in the series without AF in the reactor.

The AF had no significant effect on biogas production. In contrast, a significant effect of EMR was observed in the case of high initial COD ranging from 4.0 to 8.0 g COD/dm^3 in series II. The effect of AF on methane content in biogas was noted in variants with initial COD from 6.0 to 8.0 g COD/dm^3, whilst EMR had no significant effect on biogas composition.

The technological solutions applied in the experiment had no significant effect on the effectiveness of nitrogen compounds removal, whereas the effectiveness of phosphorus compounds removal exceeded 90% irrespective of AF composition. No effect of EMR was found on the reduction in TP concentration.

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