УДК 628.35

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# HOW PRESENCE OF SOME PHARMACEUTICALS CAN AFFECT THE PRODUCTION OF BIOGAS AT ANAEROBIC DIGESTION PROCESS

**INTRODUCTION.** During the last years, the occurrence of pharmaceuticals in aqueous media has become of interest for the protection of the environment, mainly due to their harmful effects on humans and ecosystems. After consumption, pharmaceuticals are partially metabolized in the body and their metabolites, as well as unchanged parent compounds are excreted predominantly in the urine from the body. In addition, expired pharmaceuticals are often inappropriately disposed of in toilets flushing, or are thrown into the drain [1]. According to British data one up to two thirds of unused pharmaceuticals ends up in landfills for household waste and up to fifth in the toilet [2]. It is understood that the given substances have occurred in the waste water over several decades, but a big attention is given to them only during the last years, probably because a new analytical procedure for their identification even at very low concentrations was developed.

Pharmaceuticals for the treatment plant can be removed from the wastewater using various techniques, such as oxidation or anoxic degradation, sorption to sewage sludge, anaerobic fermentation and by similar processes. The elimination of many substances from the waste water is often not the result of their degradation in the cleaning process, but the important role is also covered by process of sorption (particularly lipophilic) to the primary or excess activated sludge. Thus sorbet pharmaceuticals are diverted along with the sludge from the water into the sludge line, which is usually (in larger WWTP) undergoing the process of anaerobic fermentation.

***Anaerobic fermentation.*** Anaerobic fermentation (AF) is the process of decomposition of the biodegradable organic compounds under oxygen deficiency, a number of cultures of microorganisms. The main benefits of anaerobic fermentation is to reduce the amount of disposing of sludge, increasing its quality, decomposition of organic compounds present in the sludge and biogas production, respectively its energy use. Temperature is one of the important parameter that affects the rate of biological processes, and therefore the process of the AF. In general, with increasing temperature also the rate of running processes increases. By the change of the temperature, a change of representation of each type microorganism (MO) occurs, which may disturb the equilibrium process. To properly maintain process stability is essential to ensure a constant temperature. The shorter the residence time and lower the biomass concentration in the reactor, the more dangerous temperature changes occur. It is necessary to ensure long-term adaptation of biomass and possibly new inoculation by each change of the temperature. Depending on the temperature, we distinguish three regions of methanogenesis, where it is possible to operate anaerobic reactors, namely: psychrophilic (20 °C), mesophillic (35-40 °C) and thermophilic (55 °C). Psychrophilic area is relatively rarely used in technical practice. Mesophilic AF is one of the most used methods for the purification of primary and secondary sludge from wastewater treatment plants. However, as a result of increased requirements for treatment of sludge (hygienisation, drainage, storage and reduction of the quantity of sludge), mesophilic processes are often replaced by thermophilic processes [3]. Thermophilic AF compared to mesophilic process delivers acceleration of biochemical reactions, a greater degree of hygienisation and higher efficiency decomposition of organic matter [4]. However, thermophilic fermentation may be more sensitive to change of operating conditions such as temperature, load and characteristics of the organic sludge inflow [5].

***Investigational pharmaceuticals.*** Pharmaceuticals belong to pharmaceutical compounds, comprising an active substance and excipients which regulate the

195

pharmaceutical dosage form capable of problem-free use (tablet, syrup, ointment). The use of drugs is increasing due to the discovery of new compounds, population growth, improving quality of life, aging and the changing age structure of the population [6, 7]. Due to the frequency of pain and diseases of microbial origin among the world's most widely used pharmaceuticals in the human population include analgesic - antipyretic medicaments and antibiotics.

*Analgesics* are ancillary painkillers, divided into a narcotic analgesic, non-narcotic analgesics and non-steroidal anti-inflammatory medicaments (NSAIDs). They have a broad effect on the peripheral and central nervous systems, and are used to relieve pain of almost all diseases [8]. Consumption of analgesics in modern industrial societies is on the first place based on the medicaments volumes. Also thanks to the expansion of OTC pharmaceuticals, upward trend continues [9]. The most prescribing medicaments in terms of tolerance and the relatively good efficiency include derivatives of propionic acid and derivatives of acetoacetate such as *diclofenac*. However, diclofenac together with *ibuprofen* lead the worldwide consumption [10]. Among opioid analgesic used to treat moderate to severe pain we include for example *tramadol*.

*Antibiotics* or antimicrobial pharmaceuticals can kill bacteria or prevent their growth. They treat infections in humans, animals and sometimes plants. Not all are effective against all types of bacteria. There are over 15 different classes of antibiotics that differ in chemical structure and in their effect against bacteria. The antibiotic may be effective against one type of bacteria or against several types of bacteria. Resistance to these medications is increasing especially resistance mutations [11-12]. Slovakia has higher intake of antibiotics (23.6 mg/day.1000 inh. in Slovakia, 19.0 mg/day.1000 inh. in the Czech Republic, and only 13.8 mg/day.1000inh. in Hungary). The Netherlands has the lowest consumption (10.8 mg/day.1000 inh.), while the highest consumption was identified in Greece (32.0 mg/day.1000 inh.) [13].

*Anticonvulsants are* in addition to the main indication for the treatment of epilepsy and relatively good effect of chronic pain. Some of them are used in the treatment of headache. Among the best-known representatives of the antiepileptic pharmaceuticals include *carbamazepine*, used to treat some types of epileptic seizures, certain neurological diseases (e.g. facial pain disorders), and certain mental illnesses [14].
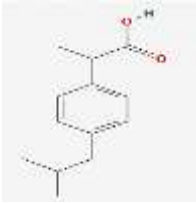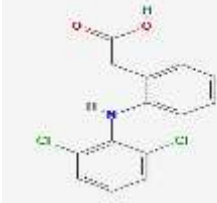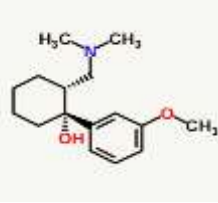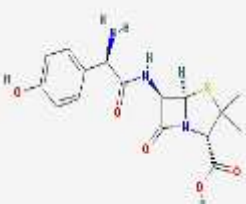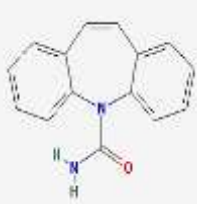
*Objectives.* In general there is limited information about the effect of pharmaceuticals on anaerobic fermentation. We decided to study the influence of selected pharmaceuticals (diclofenac, tramadol, ibuprofen, carbamazepine and amoxicillin) for the production of biogas in the process of mesophilic and thermophilic anaerobic fermentation and monitoring of their inhibitory effect.

## MATERIAL AND METHODS

*Chemicals.* Monitoring of biogas production was realized by a series of methanogenic tests for five different pharmaceuticals: diclofenac (DCF), amoxicillin (AMX), carbamazepine (CRB), ibuprofen (IBP) and tramadol (TRM). Initial concentrations of selected pharmaceuticals were 10 µg/l (index 1) respectively 500 µg/l (index 2), and they were selected according to their amount on real WWTP. Deionized water was used for their preparation. Structural formula and molar mass (M) of the selected compounds are in Table 1.

*Experiment.* The glass bottles with a septum cap with a capacity of 0,5 litres were used for methanogenic tests and were filled with conditioned mesophilic (37 °C) and thermophilic (55 °C) sludge from a laboratory model. The working volume of glass bottles was 0,33 litres. The stabilized slurry was dosed in an amount such that a final concentration of about 1 g/l. Before the test, the bottles were tempered for a given condition and then added to the bottles of selected pharmaceuticals. Substrate which provided biogas production was solution of a mixture of g-phase, urea, acetate, glucose and $NaHCO_3$. At the beginning and the end of the test we measured the pH, volatile solids VS and concentration of COD. The biogas production was daily investigated by volume measurement method.

Table 1 - Compounds of different pharmaceuticals groups [15].

| | Compounds | | |
|---|---|---|---|
| Analgetic | Ibuprofen | Diclofenac | Tramadol |
| M (g/mol) | 206,28 | 296,15 | 263 |
| Structural formula | | | |
| Antibiotic | Amoxicilin | Antiepileptic | Carbamazepine |
| M (g/mol) | 365,4 | M (g/mol) | 236,27 |
| Structural formula | | Structural formula | |

**RESULTS AND DISCUSSION**. To define the influence of pharmaceuticals on biogas production we prepared more than 150 methanogenic tests with 5 compounds from three therapeutic classes: analgesics, antibiotics, and antiepileptic. Monitoring of the impact of pharmaceuticals was implemented via methanogenic series of tests at two temperature regions at 37 °C and 55 °C. All methanogenic tests were carried out in triplicate:

- the reference tests with and without sludge substrate to define a desired endogenous production of biogas (ENDO),
- three parallel experiments with sludge and the substrate (SS), in which we determined the biogas production in the absence of pharmaceuticals,
- three parallel experiments with sludge and the substrate concentration in the selected compounds.

For illustration we present the figure 1 which shows the dependence of the total production of biogas from time to test with ibuprofen at a concentration of 500 µg/l (IBP2) at 37 °C. For each compound we calculated the average individual biogas production values. Final values in the case of ibuprofen (500 µg/l) can be seen on the second figure.
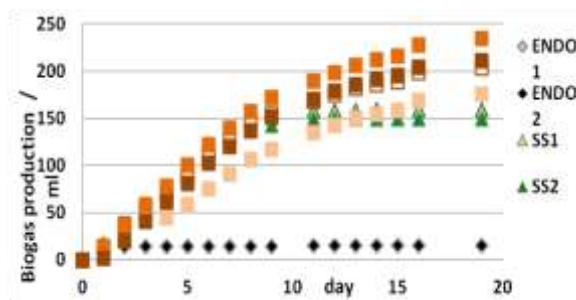


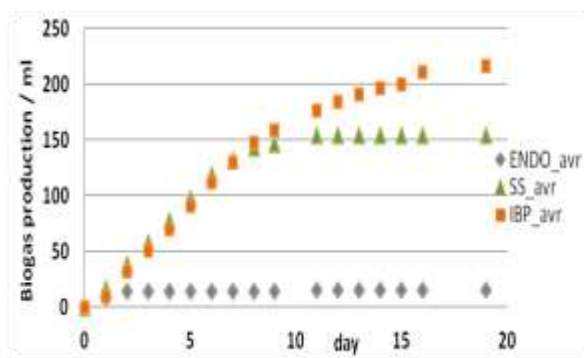Fig. 1. The total production of biogas with ibuprofen 500 µg/l in mesophilic conditions



Fig. 2. The average production of biogas with ibuprofen 500 µg/l in mesophilic conditions

The production of biogas had an increasing trend with time. The addition of 500 µg/l of ibuprofen to a mixture of sludge and the substrate caused quite a significant increase in biogas production (215 ml) compared to references by which the

**197**

maximum average value was 150 ml. In this way, we conducted a set of tests using all the test pharmaceuticals for different concentrations.

*Comparison of the total cumulative biogas production.* The figure 3 and 4 offer overall comparison of realized laboratory tests. They show the average of biogas production in the different assays and different times throughout the course of the process. Average SS1, SS2 and SS3 represent the average of all samples without compounds and other considerations will serve as a reference state.
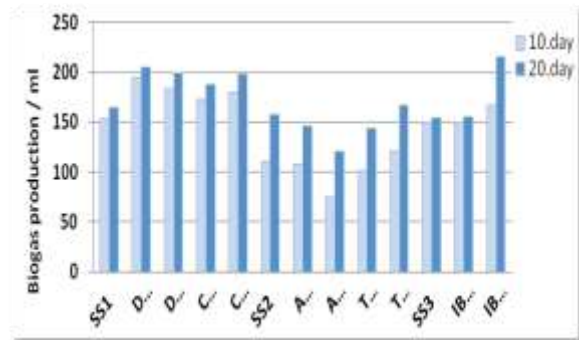


Fig. 3. Comparison of the total production of biogas for different pharmaceuticals in mesophilic condition

The lowest biogas production after 10 days was observed during mesophilic conditions with amoxicillin at high concentration of 500 µg/l (AMX2). On the other side the highest biogas production after 10 days was observed for diclofenac 10 µg/l (DCF1) followed by diclofenac 500 µg/l (DCF2) and carbamazepine in both concentrations (CRB2 and CRB1). Other pharmaceuticals in their tests produced amount of biogas, which nearly corresponds to the reference samples without the addition of drugs for which biogas production amounted to SS1=152 ml, SS2 = 110 and SS3 = 150 ml. After 20 days, the lowest biogas production was measured again for amoxicillin at high concentration (AMX2). The highest production at the end of tests had ibuprofen 500 µg/l (IBP2, over 210 ml), followed by diclofenac and carbamazepine at both concentration (DCF1, DCF2, CRB1 and CRB2, approximately 200 ml). Other pharmaceuticals produced biogas after 20 days at about 150 ml.
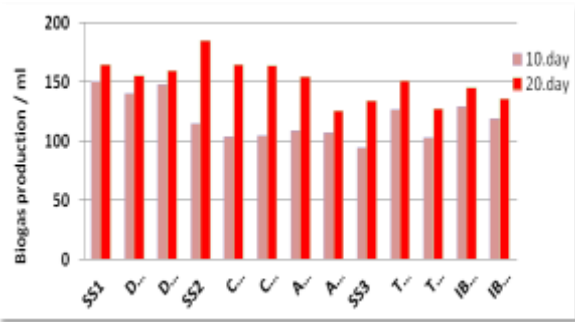


Fig. 4. Comparison of the total production of biogas for different pharmaceuticals in thermophilic condition

The highest biogas production (nearly 150 ml) during thermophilic conditions was observed similarly as during mesophilic conditions after 10 days and for diclofenac 500 µg/l (DCF2) and diclofenac 10 mg/l (DCF1). The lowest production was achieved for tramadol 500 µg/l (TRM2) followed by carbamazepine and amoxicillin in both concentrations (CRB1, CRB2, AMX1 and AMX2). At the end of the process (after 20 days) biogas quantity above 150 ml was achieved for carbamazepine and diclofenac in both concentrations (CRB1, CRB2, DCF1 and DCF2). The lowest production was reached with tramadol and amoxicillin at concentrations of 500 µg/l (TRM2 and AMX2).

**Inhibitory effect.** The comparison of the effect of pharmaceuticals on the actual production of biogas through the measurement of inhibition is provided at figure 5. To calculate the rate of inhibition I, we used the equation (1) of the Gartiser et al. (2007):

$$I = \left(1 - \frac{V_t}{V_c}\right) \cdot 100. \qquad (1)$$

Where in $V_t$ represents the volume of biogas produced from the test bottle with the pharmaceutical, and $V_c$ is the volume of biogas from a control bottle without the pharmaceutical, but it is an averaged values of the duplicate samples.

The figure 5 clearly shows that only amoxicillin at both concentrations (AMO1, AMO2) and tramadol at low concentration (TRM1) had an inhibitory effect on the process during the mesophilic conditions. During thermophilic conditions, carbamazepine and amoxicillin in both concentrations (CRB1, CRB2, AMO1, AMO2) as

well as high concentrations of tramadol (TRM2) had an inhibitory effect. Other pharmaceuticals had a stimulatory effect on the process. The pharmaceutical with highest stimulation effect at 37°C was diclofenac in both concentrations (DCF1, DCF2). For 55 °C it was tramadol in low concentrations (TRM1) followed by ibuprofen at high and at low concentrations (IBP1, IBP2). The tramadol 10 µg/l at 37 °C and ibuprofen almost did not affect the production of biogas.
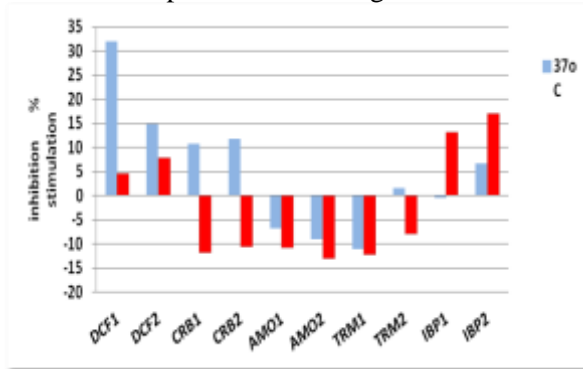


Fig. 5. Average stimulation/inhibition caused by various pharmaceuticals on biogas production

**CONCLUSION.** In our study, we examined the impact of selected pharmaceutical compounds on the production of biogas in terms of mesophilic and thermophilic anaerobic fermentation. The above results show the following main elements:

- drugs act more incentive for biogas production during the mesophilic conditions compared with thermophilic (diclofenac, carbamazepine),
- with increasing concentrations of the compounds, the effect of the pharmaceuticals on biogas production was almost unchanged (except for carbamazepine, for which the incentive effect changed to the inhibitory effect with the increase in concentration),
- an antibiotic (amoxicillin) caused a complete inhibition of the process of anaerobic fermentation, which can be explained by the fact that in the case of its use for the human body the bacteria are destroyed or respectively their growth is prevented.

Very interesting result is that some pharmaceuticals can have stimulation effect on the production of biogas. Finally, we can conclude from the presented results, that the pharmaceuticals on a small scale can influence the production of biogas in biogas plants or respectively in septic tanks, and even a very low concentrations of compounds in sludge may slightly affect these productions.

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УДК 681.54 : 628.34

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## АВТОМАТИЗАЦИЯ ПРОЦЕССА УПРАВЛЕНИЯ ОЧИСТКОЙ СТОЧНЫХ ВОД ОТ ОКИСЛИТЕЛЬНО-ВОССТАНОВИТЕЛЬНЫХ ПРИМЕСЕЙ

**Вступление.** Характерной особенностью современных металлосодержащих сточных вод промышленных предприятий является многокомпонентность состава, для которой характерны высокие концентрации загрязнений, их значительные колебания, наличие широкого спектра органических примесей (поверхностно-активных веществ (ПАВ), фенолов, эмульгированных примесей, нефтепродуктов), минеральных солей и комплексообразующих соединений. Многокомпонентность крайне негативно влияет на процессы очистки сточных вод. Для очистки таких стоков применяют введение реагентов, способствующих соосаждению металлов, сорбции органических примесей, разрушению комплексов, укрупнению мелких частиц (коллоидов), окислению или восстановлению примесей. В частности, щелочи используются для осаждения тяжелых металлов, кислоты – для подкисления очищенных сточных вод до нейтрального pH перед сбросом в канализацию или водоем. Окислители применяются для разрушения цианидов и органических примесей, восстановители – для обезвреживания такого токсичного элемента, как шестивалентный хром [1-3].

Основными способами воздействия на окислительно-восстановительные процессы очистки промышленных сточных вод является регулирование pH и окислительно-восстановительного потенциала (Eh) путем дозирования различных разнотипных реагентов: кислот, щелочей, окислителей или восстановителей. В то же время, окислители или восстановители, которые дозируются для регулирования Eh, в силу своих химических свойств одновременно изменяют также величину pH среды. Последующая корректировка величины pH вызывает обратный сдвиг величины Eh. Кроме того, в процессе протекания химических реакций также происходит изменение pH и Eh. Все это вызывает значительные трудности в поддержании оптимальных значений этих параметров, требует введения значительных количеств реагентов, а в ряде случаев делает невозможным достижение требуемых величин pH и Eh при использовании систем автоматического регулирования [4]. Разра-

**200**