ANOXIC AND ANAEROBIC WASTEWATER TREATMENT IN PRESENCE OF AROMATIC HYDROCARBONS

B. Mrowiec, L. Przywara and M. Kuglarz

University of Bielsko-Biala, Willowa 2 Street, Bielsko-Biala 43-309, Poland
(E-mail: bmrowiec@ath.bielsko.pl; *l.przywara@ath.bielsko.pl; mkuglarz@ath.bielsko.pl)*

Abstract Advance biological wastewater treatment is performed in various ORP conditions including anaerobic, anoxic and oxic processes. For removal of specific industrial and petrochemical contaminants such as: aromatic hydrocarbons (BTX), the anaerobic treatment is recommended as the adequate alternative for their removal. Anaerobic treatment process is well known as an efficient method to degrade high strength wastewater. For investigations of the treatment processes in laboratory conditions, anoxic reactor of the 5 L volume working on the HRT value of 20 h as well as anaerobic reactor of the 2,5 L and the value of HRT 72 h and 144 h were used. The concentration of aromatic hydrocarbons in municipal wastewater amounted to between 1.0 to 12.0 mg/L. A moderate negative influence of these compounds on COD removal in anoxic and anaerobic processes has been shown.

Keywords aromatic hydrocarbons, BTX, biochemical treatment, anoxic conditions, anaerobic wastewater treatment

INTRODUCTION

The Enhanced Biological Nutrients Removal Processes (EBNRP) are working according to many different schemes and technologies of various oxidation – reduction conditions applied. Biological processes of sewage treatment are aiming at compliance with the present obligatory standards, the required removals degree of organic matter, nitrogen and phosphorus. Due to the problems with energy costs; now researchers are forced to find new technologies with lower energy requirements. The solution is to apply treatment processes without oxygen demand, as well as anoxic and anaerobic processes.

The application of anaerobic wastewater treatment can be found in 1890 as the “septic tank” for domestic wastewater treatment and is often used even today. It was further developed and patented in England in 1895 and in the USA in 1894 and 1897. The best known, even in our days, is the Imhoff tank. In both technologies, the influent has very poor contact with the microorganisms, so the efficiency of soluble matter removing is very limited. The most popular anaerobic technology running in moderate climates is the upflow anaerobic sludge bed (UASB) reactor (Fdz-Polanco et al. 2009).

Reviews of anaerobic processes encompasses both fundamental and applied research performed in this area. The review is subdivided into a number of sections including microbiology, biotransformation of toxic and recalcitrant compounds, toxicity, model development, reactor systems, municipal solid waste treatment and new methods for testing of anaerobic processes. In the past decade, an increased research on the application of anaerobic technology for treatment of various types of industrial wastewaters, such as those from food processing, textile industry, paper and pulp industry was observed (Rumana et al., 2000; Pantea and Romocea, 2008). It was stated that high rate anaerobic systems represent low cost and sustainable technology for industrial wastewaters treatment; because of its low construction, operation and maintenance cost, small land requirements, low excess sludge production and production of biogas.

A sequential anaerobic-aerobic treatment system successfully treated (biochemical oxygen demand removal up to 99 %) an oil shale ash leachate containing phenolic compounds and high sulfur concentrations. The degradation of organic compounds in the anaerobic stage was mainly the result of sulfur reduction and the phenols were primarily removed in the aerobic stage. By combining an anaerobic fixed-bed upflow column inoculated with an anaerobic mixed culture capable of reductive dechlorination of PCE with another column inoculated with aerobic bacteria have been achieved complete degradation o PCE. A two-stage system composed of a methanogenic fluidized-bed granular activated carbon bioreactor fed with 2,4-dinitrotoluene (2,4-DNT) and ethanol and a batch activated sludge reactor fed with 2,4-diaminotoluene (the major product of the anaerobic biotransformation of 2,4-DNT) resulted in complete mineralization of 2,4-DNT (Pavlostathis et al., 1996).

Application of anaerobic systems for municipal sewage treatment is so far very limited. The predominant reason given for that, is that municipal sewage are too weak (to low BOD or COD) to maintain high biomass (in the form of granules – suspended solids or fixed film) content in reactor. There are however, some successful examples in pilot and full scale. Orozo (1997) investigated a full scale anaerobic baffled reactor (AnBR) for the treatment of municipal sewage of an average BOD of 314 mgO_2/L and a hydraulic retention time of 10.3 hours, (organic loading rate 0.85 $kg/m^3 \cdot d$). The removal efficiency amounted to 70%; but it has to be stressed that the process was run at very low temperature between 13 and 15 ^oC. Treatment of domestic wastewater in a UASB and two anaerobic hybrid (AnH) reactors was conducted by Elmitwalli et al. (1999) at a temperature of 13 ^oC. For pre-settled wastewater treatment, the AnH reactors removed 64 % of total COD, which was higher than the removal in the UASB reactors.

Aromatic hydrocarbons (BTX)

In wastewater treatment plant (WWTP) the presence of different industrial contaminants are stated. Among various substances the monoaromatic hydrocarbons (BTX) are found very often. BTX can be discharged with industrial wastewater, from small factories as well as public utilities and domestic sewage, (Escalas et al., 2003). Own research results and the literature dates presents a quite common occurrence of aromatics hydrocarbons in municipal wastewater. The BTX concentrations are varying in the range of 0 to 933 µg/L. Toluene is the compound most often measured in raw wastewater (Melcer et al. 1992; Hsieh et al. 1993; Bell et al. 1993; Melcer 1994; Suschka et al. 1996; Escalas et al. 2003; Kaleta, 2007).

BTX are removal during wastewater treatment processes by biodegradation, sorption and stripping to the atmosphere. But the presence of some hydrocarbons was detected in the effluent. It means that some of aromatic compounds are not completely removed in the wastewater treatment process and they can have a more or less negative effect on biological wastewater treatment processes.

The literature dates presents that biodegradation is the main way of BTX removal in wastewater treatment process. Fuchs (2008) explains four types of aromatic metabolism. The aerobic aromatic metabolism is characterized by the extensive use of molecular oxygen as cosubstrate for oxygenases, which introduce hydroxyl groups to facilitate the oxidative cleavage of the ring. Most importantly, the aromatic ring is cleaved by dioxygenases. Under microaerobic conditions, facultative aerobes use another so-called hybrid type of aerobic metabolism of benzonate , phenylacetate, and anthranilate (2-aminobenzonate). This methabolism does not require oxygen for ring cleavage. All intermediates of these pathways are coenzyme A (CoA) thioesters.

Dearomatization is catalyzed by an oxygenase/reductase acting on benzylo-CoA, phenylacetyl-CoA, and 2-aminobenzoyl-CoA, respectively, followed by an oxygen – independent ring cleavage. In anoxic conditions aromatic compounds are metabolized by facultative aerobes and phototrophs in the absence of oxygen in a purely reductive rather than oxidative process. Essential to anaerobic aromatic metabolism is the replacement of all oxygen-dependent steps by an alternative set of reactions and the formation of different central intermediates. These pathways involve a series of unprecedented enzymes. Notably, two-electron reduction of the aromatic ring of benzoyl-CoAis driven by the hydrolysis of two molecules of adeno-sine triphospate (ATP). The cyclic, nonaromatic product formed becomes hydrolytically opened and is finally oxidized to three molecules oh acetyl-CoA. Another reductive metabolism is found in strict anaerobes. Here again, benzoyl-CoA is a central intermediate of aromatic metabolism. However, when one considers growth of strict anaerobes on benzonate, an energetic problem becomes evident: Facultative aerobes, such as denitrifyers and phototrophs, spend four ATP equivalents to active benzoate as CoA thioester (two ATP equivalents) and to reductively dearomatize the ring (another two ATP equivalents). Their energy metabolism, anaerobic respiration, such as nitrate respiration, yields many more than four ATP equivalents per one benzoate metabolized; phototrophs conserve energy by photophosphorylation. In contrast, strict anaerobes gain fewer than four ATP equivalents out of one benzoate, which is metabolized via three molecules of acetyl-CoA plus one CO_2. Yet, they still require two ATP equivalents for benzoyl-CoA formation. However, they cannot spend another two ATP equivalents for the reductive dearomatization of benzoyl-CoA, because otherwise their energy metabolism would be energy – consuming rather than energy – providing. The outlines of this postulated new principle of benzoyl-CoA reduction are just emerging.

This short review gives an overview of the different strategies, with a focus on the anaerobic pathways. It does not cover the classic aerobic pathways and other important aspects, such as transport, regulation of enzymes, transcriptional control, genetic organization, distribution of the pathways, and ecological, evolutionary, and applied aspects (Fuchs, 2008).

This paper describes a series of laboratory tests of anoxic and anaerobic wastewater treatment processes that were conducted to estimate the impact of BTX on the biological treatment process. Our main objective was to find out if there was a difference in COD removal in anoxic activated sludge process and psychrophilic anaerobic digestion in presence of BTX in various concentrations.

MATERIALS AND METHODS

The laboratory investigations of the anoxic treatment process have been performed with the use of both real activated sludge and municipal wastewater, taken from a municipal treatment plant in Bielsko-Biala. The treatment plant was designed and operated for enhanced biological nitrogen and phosphorous removal. Fifteen batch series were carried out in the laboratory anoxic reactor, 5 L in volume (Fig.1). The content of activated sludge (TSS) was maintained at about 5 g/l and concentrations of BTX in treated wastewater were in the range of 0.25 and 2.4 mg/L of each of the compounds. The real concentration of BTX was measured at the beginning of consecutive experimental runs. The hydraulic retention time (HRT) was 20 h. The contents of the reactors during anoxic treatment process were continuously mixed by the application of slow mixing devices.

The investigations of the anaerobic treatment process have been performed with the use anaerobic sludge acclimatized to metanogenic conditions and municipal wastewater and taken from a municipal treatment plant in Zywiec and Tychy. The treatment plants ware designed and operated for enhanced biological nitrogen and phosphorous removal, too. Fifteen batch series were carried out in the psychrophilic anaerobic reactor, 2,5 L in volume. The HRT amounted to HRT 72 h and HRT 144 h. The content of activated sludge (TSS) was about 0,8 g/l and concentrations of BTX in treated wastewater were in the range of 0.6 and 1.1 mg/L of each of the compounds and 1.1 and 1.8 mg/L of each of the compounds for HRT value of 72 h and 144 h respectively. The contents of the anaerobic reactors ware mixed twice a day.

Table 1. General characteristic of substrates used in the experiments

Parameters and units		Municipal wastewater	
		Anoxic process	Anaerobic process
pH		6,9 – 7,4	6,6 – 7,2
ORP	[mV]	-123 - 178	-297 - 143
COD	[mgO$_2$/L]	307 –727	484 – 914
N-NH$_4^+$	[mg/L]	10 – 34	19 - 91
P-PO$_4^{3-}$	[mg/L]	2 – 11	8 - 33

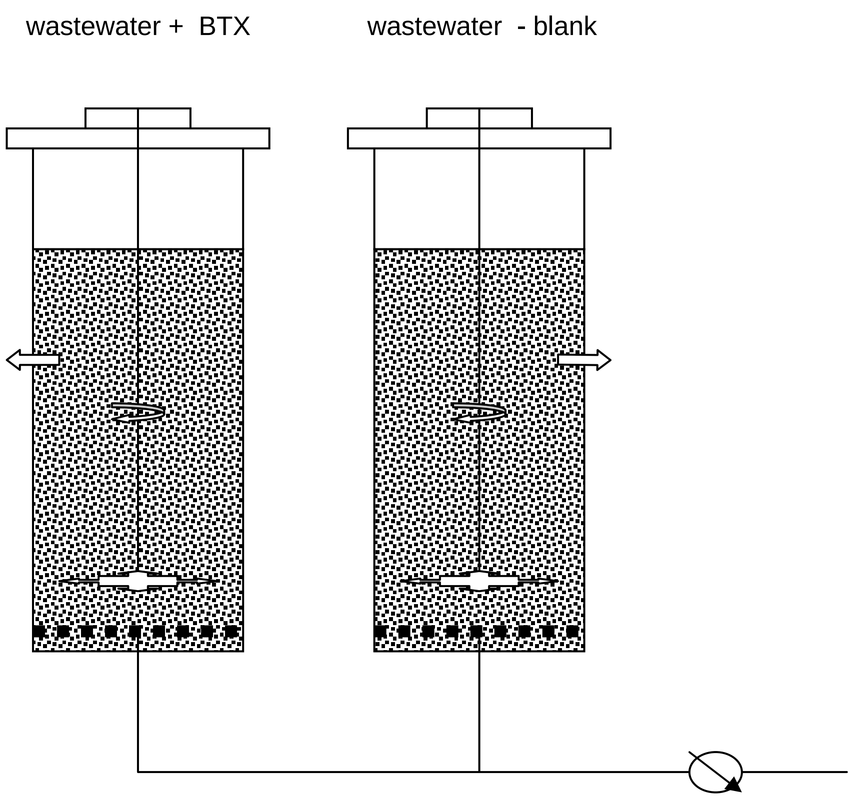

Figure 1. Laboratory reactors of the anoxic wastewater treatment

Examination of treated wastewater quality after anoxic and anaerobic, and after sedimentation for 30 minutes, included determination of: temperature, pH, COD, ORP, phosphorus (P-PO$_4^{3-}$) and nitrogen (N-NH$_4^+$). All analyses were carried out according to the Standard Methods. The BTX concentrations were determined in wastewater using the gas chromatography HP 6890 equipped with a “purge and trap system” and thermal desorption. The GC had a capillary column HP-5 Crosslinked 5% ME Siloxane (length 30 m, internal diameter 0.32 mm, film thickness 0.25 µm) and a FID detector.

RESULTS AND DISCUSSION

In raw wastewater the BTX concentrations have been measured. The compound, that has been almost always presented in wastewater and in the highest values, up to 290 µg/L, was toluene. The concentrations of benzene, o-xylene and p-xylene reached the range of between 8 and 30 µg/L. Only in one sample the concentration of o-xylene has been stated at the level 933 µg/L. For the laboratory experiments, theoretical concentrations of BTX in wastewater before anoxic treatment processes were in the range of between 0.25 to 1.25 mg/L of each compound (total BTX concentration 1.0 to 5.0 mg/L). The total concentration of the aromatic hydrocarbons used for anoxic treatment investigations amounted to from about 0.8 to 5.3 mg/L. The lower than theoretical concentration has resulted from inaccuracy of doses added and the possible losses when BTX have been introduced to the wastewater. Higher concentration was a result of BTX presence in real municipal wastewater.

Anaerobic treatment process has been performed with the use anaerobic sludge acclimatized to metanogenic in psychrophilic conditions and thus psychrophilic digestion was carried out as a preliminary process for wastewater treatment. The raw wastewater used in the experiments were characterized by the presence of total BTX concentrations ranging from 1.0 to 12.0 mg/L. In anaerobic bioreactor, the concentration of BTX working under HRT 72 regime were in the range of between 0.6 to 1.1 mg/L of each compound, whilst, for the HRT of 144 h their concentarations amounted to between 0.6 and 1.8 of each compound.

The aromatic hydrocarbons (BTX) are a part of the fraction of organic matter in wastewater, as the chemical oxygen demand (COD) determined. The dose of BTX artificially introduced into the wastewater in the laboratory experiments a little increase in the value of this parameter caused. ThOD 1 mg of benzene is 3.08 mg of oxygen, 1 mg of toluene - 3.13 mg O_2 and xylenes - 3.17 mg O_2. Following the introduction of a mixture of BTX (benzene, toluene and p-and o-xylene are added) to the wastewater from 1 to 12 mg/L as the sum of BTX, ThOD of the wastewater has been increased in the range from 3.14 to 37.7 mgO_2/L. It is believed that the increase of COD values were not significant for wastewater treatment.

The wastewater treatment in the anoxic conditions has been performend for lower organic load in the range of 0.05 and 0.12 gCOD/g·d. It was found that the presence of BTX in the biological wastewater treatment process adversely affected the efficiency of organic matter removal, determined by COD.

After anoxic treatment process, the COD values in wastewater with BTX addition have been decreased imperceptibly in contrast to raw wastewater. The COD was in the range of 210 and 647 mgO_2/L, average for each samples 490 mgO_2/L. This range of COD values was not higher than 30 % of the organic substance removal. For the blank, the average COD removal in anaerobic process was about 73 % and COD values have been between 40 and 295 mgO_2/L, on average 130 mgO_2/L. The ranges of COD values for the raw wastewater and after anoxic treatment for samples without BTX and with addition of aromatic hydrocarbons are shown in Fig. 2.

Anoxic wastewater treatment is performed before the aerobic treatment as the first or second step of biological process in treatment plants working in EBNRP technology. Therefore, high COD of wastewater in aerobic process attracts for this for increase in energy consumption and biomass production. BTX presence have the negative impact on the next aerobic process efficiency. The differences in wastewater quality and the negative effect of the aromatic hydrocarbons presence in supplied wastewater can be attributed to the higher COD values in the effluent after aerobic process. The differences in the COD values in treated wastewater both with and without BTX are clearly seen in Fig. 3. The impact of BTX in wastewater on the COD values after two steps treatment is shown in Fig. 4.

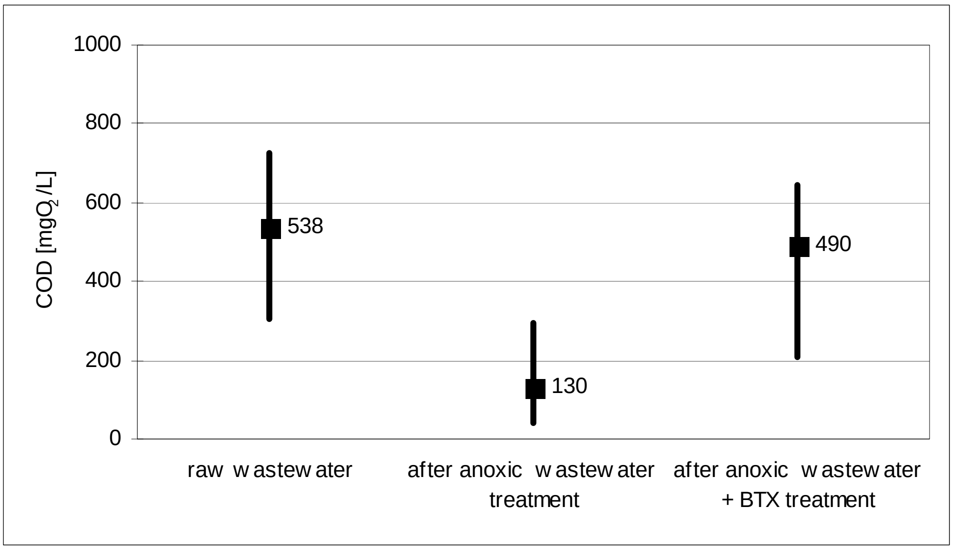

Figure 2. Decrease of COD after anoxic wastewater treatment process

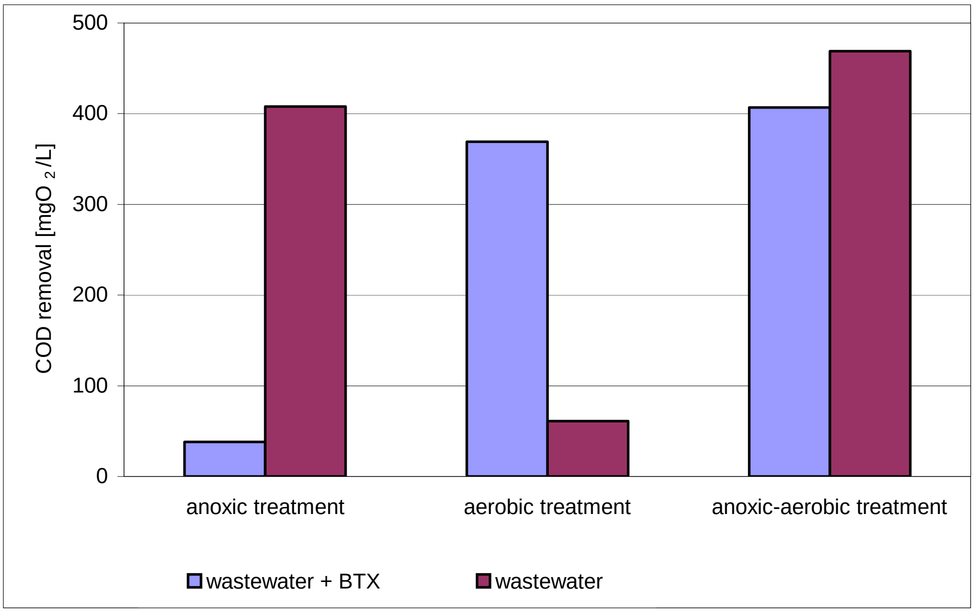

Figure 3. The average COD removal in the anoxic-aerobic wastewater treatment process

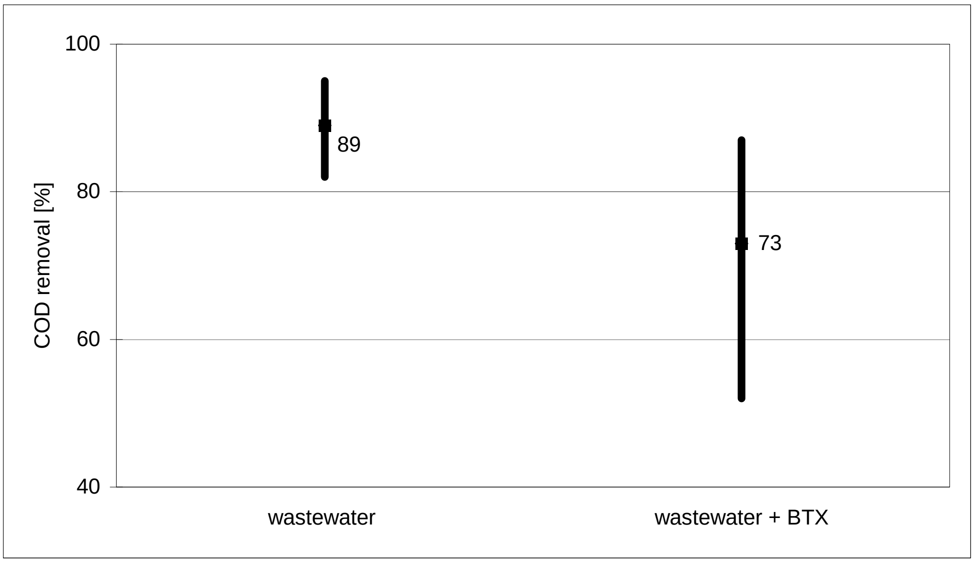

Figure 4. The COD removal in the anoxic-aerobic wastewater treatment process

Anaerobic process

The effluent COD was lower between 15 and 40 % compared to corresponding samples without BTX. The efficiency of the process carried out under anoxic-aerobic wastewater treatment, in which raw sewage were characterized by varying load of organic matter and BTX concentration at about 5,3 mg/L, was stated at the level of between 48 and 87%, on verage 73% in case of samples with BTX, wwile, COD removal of wastewater, which does not contain BTX has varied in the range from 82 to 95%, on average 89%. Decrease of wastewater treatment efficiency obtained on the basis of the COD values was about 20 %. It was found that in conditions of summary BTX concentrations above 2 mg/L significantly higher COD values of wastewater after anoxic treatment stage were recorded. Similarly, the marked increase in the COD values in the effluent due to increase of BTX concentration in the wastewater introduced to the reactor together with suspended activated sludge has been presented by Aysegul (2004).

The laboratory batch tests in anaerobic conditions (psychrophilic digestion) have shown insignificant impact of BTX on organic matter removal.

Anaerobic psychrophilic digestion was carried out as a preliminary process for wastewater treatment. The wastewater used in the experiments were characterized by the presence of BTX concentrations ranging from 0.6 to 1.1 mg/L for the reactor of HRT 72 h and from 0.6 to 1.8 for the reactor of HRT 144 h. In the conditions applied, the COD removal was achieved in a less differentiated ranges than in anoxic conditions. Essentially, the differences in wastewater quality achieved in cases of effluents from the reactor with a shorter retention time (HRT 72 h) and higher HRT (144 h) were not significant. The raw wastewater ware characterized by COD in the range of 484 and 914 mgO_2/L, on average 628 mgO_2/L. After the psychrophilic digestion with HRT 72 h, the effluent COD decreased, and varied from 333 to 466 mgO_2/L (average value 387 mgO_2/L) for samples with BTX addition. In the blank samples, COD measured fluctuated from 265 to 384 mgO_2/L (average value312 mgO_2/L). The decrease of COD values after anaerobic wastewater treatment process with HRT 72 h are shown in Fig. 5.

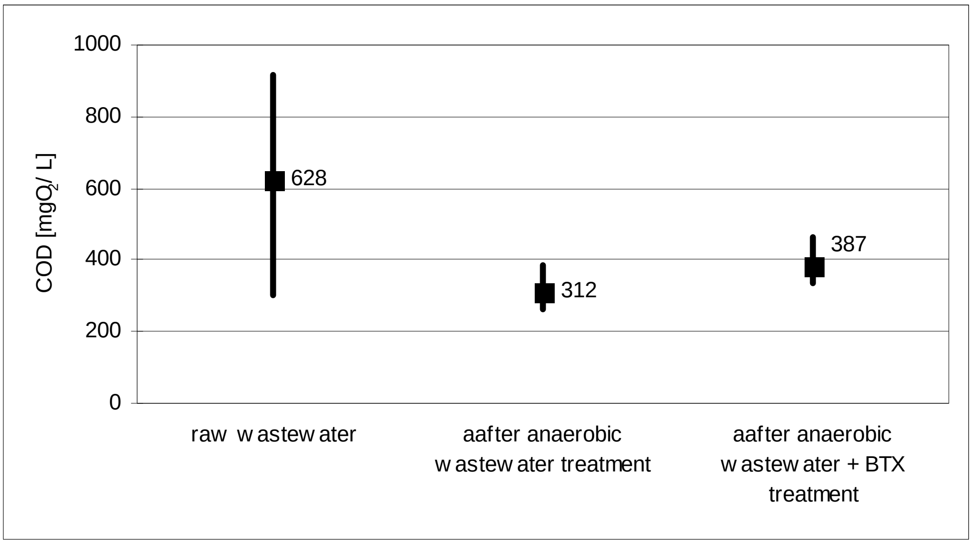

Figure 5. Decrease of COD after anaerobic wastewater treatment process with HRT 72 h

Similar relationships have been observed in the reactor with HRT 144 h. The decrease of COD values in the effluents varied in the range of 245 and 381 mgO_2/L (average value 317 mgO_2/L) for wastewater with BTX addition, and from 235 and 337 mgO_2/L (average value 293 mgO_2/L) for blank (Fig. 6).

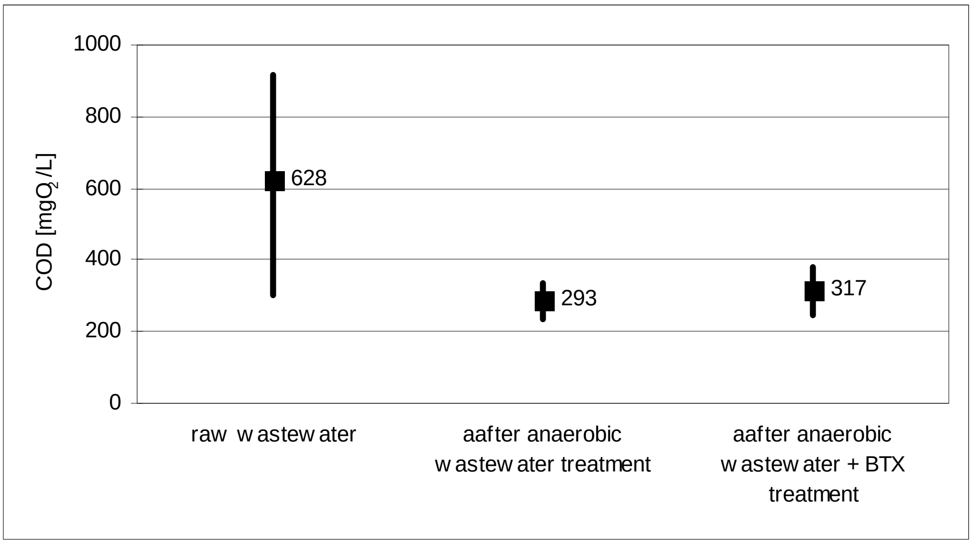

Figure 6. Decrease of COD after anaerobic wastewater treatment process with HRT 144 h

Insignificant difference between COD values after anaerobic treatment among the samples with BTX addition and without hydrocarbons probably were the results of longer retention time in contrast to anoxic process. Also, twice higher HRT (144 h) has not been important for COD removal.

The COD removal in psychrophilic digestion in the reactor with HRT 72 h varied from 27 to 49% (average value 37 %) for wastewater with BTX and from 32 to 67 % (average value 58 %) for blank samples. Slightly higher values have been obtained for the wastewater anaerobically treated in the reactor with HRT144 h, which amounted from 28 to 52 % (average value 38 %) for wastewater with BTX addition and from 37 to 71 % (average value 63 %). The efficiency of COD removal in the anaerobic wastewater treatment process with HRT 72 h and 144 h are presented in. Fig. 7.

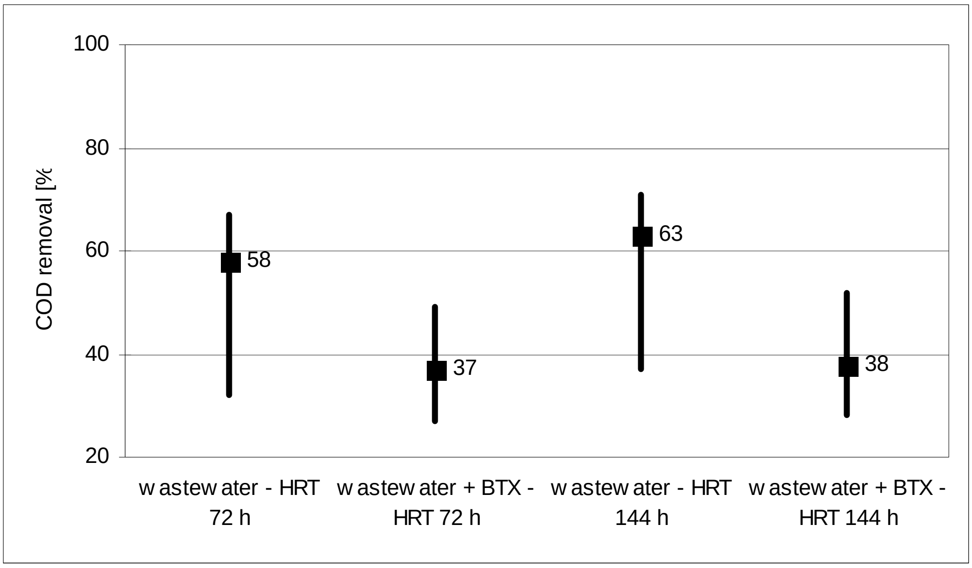

Figure 7. The COD removal in the anaerobic wastewater treatment process with HRT 72 h and 144 h

The differences in COD values in samples with BTX presence and in the blank have not influenced on the post treatment in aerobic conditions. The quality of effluents ware similar and efficiency of COD removal for all samples varied in the range of 74 and 91 %.

SUMMARY

The presence of BTX (toluene, benzene, p-xylene and o-xylene) in municipal wastewater has so far not raised sufficient attention and its problem needs more profound explanation in context of biological wastewater treatment. BTX in concentrations above 2 mg/L significantly increased COD values of wastewater after anoxic treatment process. A clear, negative impact of the BTX presence in wastewater due to the removal of organic matter was observed in almost every cases of the low-loaded organic pollutants used. In the presence of increased concentrations of BTX (up to 5.3 mg/L) after anoxic conditions the lowest COD removal efficiency have been obtained. In comparison to samples without the BTX addition, the lower COD values were measured in effluent. The results of this study indicated the feasibility of anoxic and anaerobic conditions for the wastewater treatment containing BTX.

Acknowledgements
This work was funded by the National Science Centre, Poland (grant N N523 742940).

REFERENCES

Aysegul P. (2004). The effect o benzene, toluene and o-xylene on COD removal in an aerobic fluidized bed reactor utilizing acetic acid as the main carbon source. *Environmental Engineering Science* 18 (6), p. 337-345.

Bell, J., Melcer, H., Monteith, H., Osinga, I., and Steel, P. (1993). Striping of volatile organic compounds at full-scale municipal wastewater treatment plants. *Water Environment Research* 65 (6), p. 708-716.

Elmitwalli, T. A., Zandvoort, M. H., Zeeman, G., Bruning, H., Lettinga, G. (1999). Low temperature treatment of domestic sewage in Upflow Anaerobic Sludge Blanket and Anaerobic Hybrid Reactors. *Water Science Technology*, 39 (5), p. 177-185.

Elmitwalli, T. A.; Zandvoort, M. H.; Zeeman, G.; Bruning, H.; and Lettinga, G. (1999). Low temperature treatment of domestic sewage in Upflow Anaerobic Sludge Blanket and Anaerobic Hybrid Reactors. *Water Science Technology*, **39**, (5), 177-185.

Escalas, A., Guadayol, J., Cortina, M., and Rivera, J. (2003). Time and space patterns of volatile organic compounds in a sewage treatment plant. *Water Research* 37, p. 3913-3920.

Fdz-Polanco F., Perez-Elvira S.I., Fdz-Polanco M. (2009). Present and perspectives of anaerobic treatment of domestic sewage. *Desalination and Water Treatment* 4, p. 161-167.

Fuchs G. (2008). Anaerobic metabolism of aromatic compounds. *Ann. N.Y. Acad. Sci.* 1125, p. 82-99.

Hsieh, Ch., Babckock, R., Stenstrom, M. (1993). Estimating emissions of 20 VOCs II: Diffused aeration. *Journal of Environmental Engineering* 119 (6), p.1100-1118.

Kaleta, J. (2007). Niebezpieczne zanieczyszczenia organiczne w środowisku wodnym. *Zeszyty Naukowe, Południowo-Wschodni Oddział Towarzystwa Inżynierii Ekologicznej z siedzibą w Rzeszowie, Polskie Towarzystwo Gleboznawcze oddział w Rzeszowie*. Zeszyt 9, p. 31-40.

Melcer, H., Bell, J., Thompson, D. (1992). Predicting the fate of volatile organic compounds in municipal wastewater treatment plants. *Environ. Sci. Technol*. 25 (4-5), p. 383-389.

Melcer, H. (1994). Monitoring and modeling VOCs in wastewater facilities. *Environ. Sci. Technol*. 28 (7), p. 328-335.

Orozco A. (1997). Pilot and full scale anaerobic treatment of low strength wastewater at sub-optimal temperature (15^{o}C) with a hybrid plug flow reactor. Proceedings of 8th International Conference on Anaerobic Digestion, Sendai, Japan **,** 2, p. 183-191.

Pantea E.V., Romocea T. (2008). Thermophilic anaerobic wastewater treatment. *Protectia Mediului, Analele Universitatii din Oradea* 8, p. 454-458.

Pavlostathis S.G., Misra G., Prytula M., Yeh D. (1996). Anaerobic processes. Literature Review. *Water Environment Research* 68 (4), p. 479-497.

Rumana R., Somchai D., Kannitha K. (2000). Anaerobic processes. Literature Review, *Water Environment Research*, 72 (5), p. 576-656.

Suschka, J., Mrowiec, B., Kuszmider, G. (1996). Volatile organic compounds (VOC) at some sewage treatment plants in Poland. *Wat. Sci. Tech*. 33 (12), p. 273-276 .