INFRASTRUKTURA I EKOLOGIA TERENÓW WIEJSKICH
INFRASTRUCTURE AND ECOLOGY OF RURAL AREAS

Nr IV/3/2016, POLSKA AKADEMIA NAUK, Oddział w Krakowie, s. 1593–1602
Komisja Technicznej Infrastruktury Wsi

DOI: http://dx.medra.org/10.14597/infraeco.2016.4.3.119

SUITABILITY OF SEWAGE FROM THE PRODUCTION OF ORGANIC POLYMERS FOR BIOLOGICAL TREATMENT

Magdalena Frąk, Agnieszka Zadura
Warsaw University of Life Science – SGGW

Abstract

The possibility of biological treatment of sewage from the production of organic polymers was assessed. The chemical quality of raw and treated sewage (COD_{Cr}, BOD_5, ammonia nitrogen, nitrate nitrogen, total suspension, pH, chlorides and sulfates) was analyzed. The level of reduction in the analysed sewage quality indicators (%), sewage biodegradability (α) and the technical efficiency of treatment (P_{sw}) were determined. It was shown that the limited effectiveness of the treatment process results from the excessively high load of organic contaminants. The analysed sewage contains substances which do not biodegrade easily, negatively influencing the conditions for activated sludge processes in the bioreactor. The activated sludge is characterized by low biodiversity and has an insufficient structure. The treatment process requires an introduction of technological changes which will lead to a decrease in the load of sewage entering the bioreactor.

Key words: industrial sewage, biological treatment, biodegradability, activated sludge

INTRODUCTION

Contaminants making their way into water ecosystems are a major environmental problem. They are often introduced into the environment with insufficiently treated sewage. Industrial sewage, containing substances which are difficult for living organisms to assimilate or even toxic to them, poses a significant problem (Awaleh, Soubaneh, 2014; Bartkiewicz, 2006; Nasr, *et al*., 2004).

Passed on to the receiver, industrial sewage can lead to changes in the biodiversity of an ecosystem, and at the same time decelerate or impede self-cleansing processes (Krzanowski, *et al.*, 2008; Nasr *et al.*, 2004). Due to difficulties in developing highly effective treatment technology, substances which are harmful to the environment are not entirely removed from sewage. In contrast to domestic sewage, the contents of industrial sewage can vary depending on the type of business activity being carried out, the accepted water and sewage management system, and changes in the amount of effluent dependant on the production cycle (Bartkiewicz, 2006; Heidrich, Witkowski, 2005).

It is especially difficult to treat sewage from industries which make use of potent chemical substances, including those which have a harmful effect on living organisms. Sewage from the production of substrates used by the chemical industry (for the production of medicine, motor parts, textiles, etc.) often contains substances characterized by low biodegradability (Awaleh, Soubaneh, 2014; Szyprowska, *et al.*, 2011; Sadecka, 2010; Bartkiewicz, 2006; Bartoszewski, 1997). This leads not only to problems connected with their removal, but also with their assimilation by ecosystems.

Biological treatment of sewage is based on mechanisms used when removing organic contaminants in natural water ecosystems. However, the process is designed is such a way that the treatment takes places much faster and on a much smaller surface than under natural conditions. The efficiency of the process is based on two factors: a sufficient active mass of microbes (activated sludge) and ensuring a constant supply of oxygen (Sadecka, 2010; Lenart, Witkowski, 2012; Wiąckowski, 2005). The biological removal of contaminants from sewage can be more efficient and more economical than chemical-mechanical treatment. Therefore, attempts are also made at applying nature-based solutions for treating sewage of an industrial origin. Their effectiveness is, however, largely dependent on the chemistry of sewage. When adapting activated sludge to a given chemical composition, natural selection makes it possible to eliminate that which is not suited for the current conditions. A high diversity and amount of microbes ensure the effective removal of various contaminants (Budkowska *et al.*, 2012; Wiąckowski, 2005; Nasr *et al*., 2004; Eikelboom, van Buijsen, 1983). However, microflora is deficient in sewage derived from the chemical industry. This is largely due to the presence of heavy metals and toxic substances, and an improper pH (Szyprowska *et al*, 2011; Bartkiewicz, 2006; Bury *et al*, 2002). The composition of such sewage may also contain mutagenic or toxic substances.

In order to effectively reduce substances that are harmful to the environment by means of activated sludge sedimentation, it is necessary to prepare them properly. The following have to be ensured: a stable quality and quantity of sewage flowing into the bioreactor, a stable pH in the range of 69, the lack of toxic substances, the removal of emulsions and suspensions which do not bind with water, and ensuring minimal necessary contents of organic and non-organic forms of nitrogen and phosphorus (Lenart, Kowalska, 2012; Sadecka, 2010; Wiąckowski, 2005) .

Sewage created in the production process is sent to the described treatment plant where it is mixed in order to unify its quantity and chemical composition, and ensure the consistent operation of the plant. In the initial phase of treatment, sewage is neutralized (5% $Ca(OH)_2$) to a pH of 6.59.5 (the average incoming sewage has a pH of 3.7). Biological treatment then takes place in a two-stage process: in the aerobic (oxygenation 2.0-3.0 mg O_2/dm^3) and anaerobic zone. At this time, 5% H_3PO_4 is added to neutralize the pH and as a supplementary growth medium for the activated sludge. Within the bioreactor, the removal of organic and mineral nitrogen takes place as a result of nitrification and denitrification processes. After approx. 28 h of storage, the sewage passes on to a collection trough and next to secondary clarifiers. Here the process of separating the sewage from the precipitate takes place by means of sedimentation after a holding time of approx. 4.5 h. The return activated sludge is then recirculated through pipes, re-entering the biological chambers along with raw sewage (200% level of recirculation); excessive sludge finds its way to the excess sludge storage chamber, while clarified sewage flows into a collection trough. Treated sewage is then mixed with other sewage (rainwater and that from other parts of the plant) in the collection trough, from where it runs into an effluent canal, retention chamber or receiver (river). The aim of the research is to assess the suitability of the tested sewage to undergo biological treatment.

MATERIALS AND METHODS

Raw and treated sewage samples, collected from January 2010 to December 2013, were subjected to studies. pH (using the potentiometric method), COD_{Cr} (chemical oxygen demand) (dichromate method), N_{NH4} (method using Nessler's reagent), N_{NO3} (in the presence of H_2SO_4, $C_6H_4(OH)COONa$ and nitrates) and TSS (total suspended solids) (gravimetric method) were measured every 24 hours; BOD_5 (five daily biological oxygen demand) was determined twice a week. The concentration of chlorides (using the titration method with $AgNO_3$) and sulfates (precipitation method in the presence of $BaCl_2 \cdot 2H_2O$ and HCl) was determined once a week. The work makes use of monthly and annual averages for the individual measured indicators (in mg/dm^3).

A study of the structure of activated sludge was also carried out. The samples were taken from the bioreactor and then subjected to microscopic observation using an OPTA-TECH biological microscope. The analysis was carried out in accordance with methodological guidelines (Eikelboom, van Buijsen, 1983).

In order to determine the suitability of the studied sewage for biological treatment, the daily load and the biodegradability indicator of sewage α were determined. The efficiency of the cleaning process was determined based on the percentage reduction of pollutants in the analysed time period and the indicator of technical plant efficiency $P_{sw.}$

RESULTS AND DISCUSSION

Analysing the collected data on the quality of sewage from the analysed plant, a decreasing average annual concentration of BOD_5 and COD_{Cr} in raw sewage was confirmed in the period under study (BOD_5 averaging 1860 mg O_2/dm^3 in the year 2011 to 1370 mg O_2/dm^3 in 2013; COD_{Cr} averaging from 3733 mg/dm^3 in 2011 to 2768 mg/dm^3 in 2013).The values of the indicators demonstrate significant contamination of the analysed raw sewage with organic compounds. An over twice higher value of COD_{Cr} than BOD_5 indicates a dominance of organic compounds that do not undergo biological oxidation. The concentration of nitrate nitrogen in raw sewage is over six times higher than ammonium nitrogen. This suggests its adequate oxidation. However, in the summer period (June-August), there is a regular, annual increase (even of up to 30-fold) in the concentration of ammonium in effluent. This indicates disturbances in the nitrification process during treatment. It may also be connected with the regularly lower delivery of sewage in the summer months (in July and August, approx. 1/3 lower than in the winter months). The pH of incoming sewage is acidic (pH of 3.7), which is connected with the necessity of its neutralization prior to being entered into the bioreactor. However, the increased concentration of ammonium in treated sewage additionally influences an increase in pH (up to 8.7). The concentration of chlorides which are typical of pollutants of an anthropogenic origin in raw sewage is at the level of 52-105 mg/dm^3 (average of 79.3 mg/dm^3), with sulfates found in amounts of 53-197 mg/dm^3 (average of 142 mg/dm$^{3).}$ A higher concentration of pollutants was noted in the summer period.

The indicated percentage reduction of contaminants (Tab. 1) is at a very high level. The average reduction in the concentration of BOD_5 is 98.3%, while COD_{Cr} by 95.6%. The reduction of nitrate nitrogen and ammonium nitrogen are also at a very high level (99.7% and 94.6% respectively). The amount of suspended solids in the effluent decreased on average by over 31.2%, while the concentrations of chlorides and sulfates were reduced minimally, i.e. by 2.2% and 1.0% respectively. Low level of standard deviation and variance marks a stable value reduction for BOD_5, COD_{Cr}, N_{NO3}, chlorides and sulfates. The effectiveness of treatment in terms of removing organic compounds and nitrogen compounds is at a high level.

The daily load in the treated effluent was also determined for the analysed sewage (Tab. 2). The highest loads of contaminants occur in the case of sulfates and COD_{Cr}, amounting to approx. 495 kg/day. The lowest contaminant load is delivered to the rainwater canal in the form of nitrate nitrogen (3.4 kgN_{N03}/d) and ammonia nitrogen (14,4 kgN_{NH4}/d). From 2011 to 2013, the average load of COD_{Cr}, suspension, and ammonia as well as nitrate nitrogen decreased in the effluent. These data indicate that the treatment process should be directed at organic substances that are resistant to biodegradation – chlorides and sulfates. These are groups of substances the removal of which can prove to be the most problematic for the treatment plant (Bury *et al.*, 2007; Bartkiewicz, 2006; Nasr *et al.*, 2004). Wide variable of average contaminant loads allow by means of standard deviation and variance (especially for COD_{Cr}).

Table 1. Percentage reduction of contaminants shown as averages for the individual year in 2011-2013

Year	**Average reduction in pollutant concentrations [%]**						
	BOD_5	**COD_{Cr}**	**TSS**	**N_{NH4}**	**N_{NO3}**	**Chlorides**	**Sulfates**
2011	98,7	95,9	20,8	95,4	99,6	2,2	1,2
2012	98,0	95,6	43,6	94,8	99,5	3,6	1,4
2013	98,1	95,3	29,2	93,5	99,9	0,9	0,4
Numbers of sample	312	1095	1095	1095	1095	156	156
The average reduction of 3 years	**98,3**	**95,6**	**31,2**	**94,6**	**99,7**	**2,2**	**1,0**
Standard deviation [-]	0,61	0,73	8,81	6,54	0,21	1,3	0,83
Variance [-]	0,40	0,50	77,77	42,70	0,00	1,70	0,70
Coefficient of variation [-]	0,01	0,01	0,28	0,07	0,00	0,58	0,82

The determined biodegradability indicator α also indicates that substances which do not undergo biological oxidation easily are present (Budkowska *et al.*, 2012; Sadecka, 2010) . Sewage can be treated using classical biological methods when the α coefficients takes on a value lower than 2; when the value is over 2, it is likely that sewage possesses characteristics which make the proper course of physiological processes difficult for the microorganisms present in activated sludge. The α indicator determined for the analysed sewage (Tab. 3) assumed the lowest value in November 2014 (1.23), while the highest in June 2014 (3.09). The average in the individual years exceeds 2.0, which indicates that it is impossible to completely inactivate organic substances contained in sewage from the production of plastics. One ought to consider whether there may be a necessity to pre-treat sewage by chemical means (e.g. precipitation) prior to it being directed to activated sludge bioreactors.

Table 2. Values of daily contaminant loads in treated sewage.

Year	Average daily contaminant loads [kg/d]						
	BOD_5	COD_{Cr}	TSS	N_{NH4}	N_{NO3}	Chlorides	Sulfates
2011	86,5	530,3	179,2	12,9	3,3	214,4	539,8
2012	102,0	491,8	114,9	15,3	5,1	265,9	456,9
2013	90,8	461,4	108,5	15,0	1,8	350,4	489,2
Numbers of sample	312	1095	1095	1095	1095	156	156
The average load of 3 years	**93,1**	**494,5**	**134,2**	**14,4**	**3,4**	**276,9**	**495,3**
Standard deviation [-]	25,9	59,3	15,0	21,4	2,1	30,8	40,2
Variance [-]	669,4	3511,2	226,4	456,9	4,4	948,0	1614,1
Coefficient of variation [-]	0,3	0,1	0,1	1,5	0,6	0,1	0,1

Table 3. Values of biodegradability indicator of analysed sewage α

Year	Average value [-]	Minimum value [-]	Maximum value [-]	Standard deviation [-]	Variance [-]	Coefficient of variation [-]
2011	2,00	1,30	2,43	0,31	0,10	0,16
2012	2,23	1,65	2,65	0,33	0,11	0,15
2013	2,02	1,75	2,43	0,24	0,06	0,12
The average of 3 years	**2,08**	**1,30**	**2,65**	**0,29**	**0,09**	**0,14**

In addition to sewage from the production of organic polymers, other sewage (rainwater, other activities of the Plant) also finds its way into the effluent canal. This leads to difficulties when interpreting the level of the assessed indicators, as well as the efficiency level of the treatment process. Contaminants present in the sewage flowing into the storage reservoir undergo further biochemical changes, which leads to a probable decrease in their concentrations running out into the receiver. A compilation of the values of the indicators with standards is possible due to carrying out a simulation based on the assumption that the sewage derived from the Biological Treatment Plant are the only provider of sewage to the receiver. Thus, values of the technological efficiency of treatment (P_{SW}) were assessed for the individual parameters (Tab. 4). When the specified P_{SW} indicator is close to the value of 1, as in the case of the suspension, nitrate nitrogen, chlorides or sulfates, the probability of obtaining the necessary values in the runoff is very high. However P_{SW} values for BOD_5 (0.46) and COD_{Cr} (0.35) indicate a low probability of obtaining the desired concentrations. This suggests the necessity of introducing modifications in the technological system of the sewage treatment process. Moreover, the level of the P_{SW} indicator for COD_{Cr} indicates that the nature of the analysed sewage makes their biological treatment difficult due to the presence of substances which do not biodegrade easily (or are non-biodegradable) (Budkowska *et al*., 2012; Heidrich, Witkowski, 2005; Bartoszewski, 1997). The discharge of increased amounts of these types of contaminants with the sewage could pose a significant risk to the ecosystem of the receiver (i.e. river).

Table 4. Values of the technological efficiency of treatment (P_{SW})

P_{SW} [-]						
BOD_5	**COD_{Cr}**	**TSS**	**N_{NH4}**	**N_{NO3}**	**Chlorides**	**Sulfates**
0.46	0.35	0.92	0.81	0.97	0.97	0.97

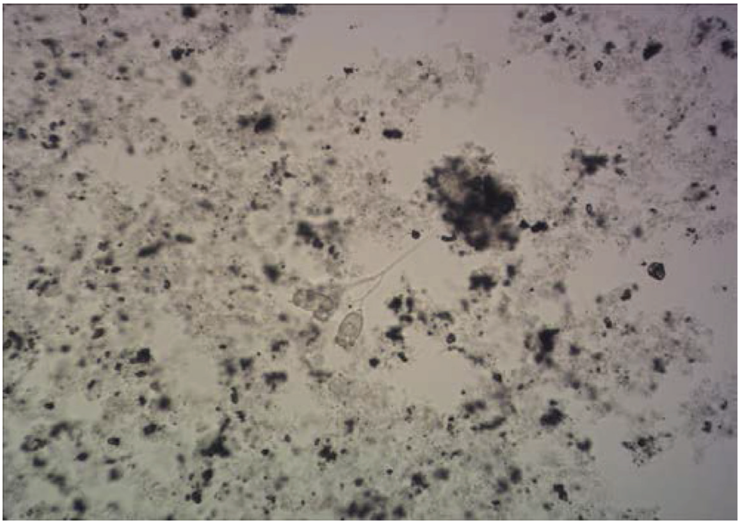

Figure 1. Form and structure of activated sludge floccules (x 200) (photo: Frąk, Zadura)

In order to confirm that the conditions for activated sludge in the bioreactor are impeded, microscopic studies of its structure were carried out. The flocculent structure typical of activated sludge was not confirmed (Eikelboom, van Buijsen, 1983). The observed floccules were characterized by an irregular shape, low cohesion and loose structure (Fig. 1), which is indicative of poor quality of the sludge. Taking into account the conclusions made on the basis of the conducted analysis regarding the quality of the studied sewage, the following may be responsible for the insufficient activity of the activated sludge: excessive sewage load and/or the presence of toxic substances.

Numerous freely occurring bacteria and individual colonies of ciliates *Carchesium sp*. were observed in the biological composition of activated sludge. Other animal organisms typical of activated sludge were not observed. The lack of *Arcella sp*. in the analysed sewage suggests a high contaminant load of the sewage flowing into the bioreactor (confirmation of data in Tab. 2). The confirmed poor biological structure moreover indicates the presence of harmful substances in the sewage (Lenart, Kowalska, 2012). The presence of attached ciliates is indicative of achieving a state of stability by the formed activated sludge, thus the stability of conditions in the bioreactor (Wiąckowski, 2005) .

The structure and biological composition of sludge point to bad conditions in the treatment process and, therefore, the limited ability of microorganisms to reduce contaminants. The observed individual colonies of protozoa indicate an improper chemical makeup of the sewage, the presence of toxic substances (or in toxic concentrations), and their insufficient oxygenation. Such a low quantity of protozoa leads to an insufficient reduction of free-swimming bacteria which are not included in the composition of activated sludge floccules, and thus do not carry out biochemical processes beneficial to the sewage treatment process. The excessive dispersion of bacterial cells can additionally be caused by excessive mixing of sewage which "breaks apart" sludge floccules.

The ratio of COD_{Cr} to BOD_5 values (α indicator) indicates that the analysed sewage from the production of organic polymers flowing into the activated sludge chamber contains many chemical compounds which do not undergo biological oxidation. The presence of toxic substances or other contaminants in toxic concentrations causes the biodiversity of the activated sludge to be severely limited. The comprehensive analysis of the physicochemical quality of the incoming sewage would make it possible to determine the factors that negatively influence the living organisms of activated sludge.

CONCLUSIONS

The analysis of the structure of activated sludge and the physicochemical qualities of sewage from the production of organic polymers suggests that the conditions for the treatment process are improper. The determined indicators reveal a dominance of chemical compounds in sewage which do not undergo biological degradation. The specific chemical composition of sewage limits the possibility of its biological treatment. The studies suggest the necessity of decreasing the contaminant load of sewage entering the bioreactor; this will improve the conditions in which activated sludge processes take place and, at the same time, also its biological structure.

In an effort to reduce the concentrations of contaminants in sewage derived from the production of organic polymers, additional technological solutions ought to be considered. Chemical pre-treatment of sewage, prior to it entering the biological treatment system, would contribute to decreasing the value of the COD_{Cr} indicator of sewage entering the bioreactor. One possibility is applying chemical precipitation, in which soluble compounds change into non-soluble forms under the influence of a reagent. It is possible that mixing sewage created in the production process with precipitation wastewater prior to its introduction into the bioreactor would lead to a decrease in the sewage load. This would make it possible to reduce the degree of sewage recirculation, as well as decreasing the values of indicators in treated sewage.

ACKNOWLEDGMENT

The authors would like to cordially thank those managing the analyzed Industrial Plant for providing access to data which made the present work possible. At their request, detailed information regarding the Plant has not been disclosed.

REFERENCES

Awaleh M.O., Soubaneh Y. D. (2014): Waste Water Treatment in Chemical Industries: The Concept and Current Technologies. Hydrol Current Res., vol5, 164. DOI: 10.4172/2157-7587.1000164

Bartkiewicz B. (2006): Treatment of industrial wastewater. (in Polish) PWN Inc., Warsaw.

Bartoszewski K. (1997): Guide exploiter sewage treatment plant. (in Polish) Polish Association of Sanitary Engineers and Technicians Inc., Poznań.

Budkowska A., Długosz J., Gawdzik J. (2012): Validation of the operations of wastewater treatment plant in Starachowice. Archv. Waste Manag. Environ. Protection, vol. 14, 3, 1-12.

Bury, S.J., Groot, C.K., Huth, C., and Hardt, N. (2002): Dynamic Simulation of Chemical Industry Wastewater Treatment Plants, Water Science & Technology 45(4–5), 355–363.

Eikelboom D. H., van Buijsen H. J. J. (1983). Microscopic sludge investigation manual. TNO Research Institute for Environmental Hygiene, 1983.

Heidrich Z., Witkowski A. (2005). Wastewater treatment plant, design, calculation examples. (in Polish) Seidel-Przywecki Inc., Warsaw.

Krzanowski S., Wałega A., Paśmionka I. (2008). Treatment of wastewater from selected food industry. (in Polish) Infrastruktura i Ekologia Terenów Wiejskich, monograph; 2008(1);

Lenart A., Kowalska A. (2012: The use of activated sludge wastewater treatment. (in Polish) Kosmos, vol. 61, 4 (297), 677-689.

Nasr F.A., Doma H. S., Abdel-Halim H. S., El-Shafai S.A., (2004): Chemical industry wastewater treatment. TESCE, vol. 30, 2, 1183-1206.

Sadecka Z. (2010: Fundamentals of biological wastewater treatment. (in Polish). Seidel-Przywecki Inc., Warsaw.

Szyprowska M., Wichowski P., Stępień P. (2011). Investigations of anaerobic wastewater treatment plants on the example of the pharmaceutical industry. (in Polish) Infrastruktura i Ekologia Terenów Wiejskich. Vol. 07, 155-168.

Wiąckowski K. (2005): Biology of activated sludge. In: The activated sludge: biology and microscopic analysis. (in Polish). Impuls Inc., Kraków.

Corresponding author: Eng. Magdalena Frąk PhD
e-mail: magdalena_frak@sggw.pl
Warsaw University of Life Sciences (SGGW),
Department of Environmental Improvement
Nowoursynowska Str. 166, 02-787 Warsaw;

Eng. Agnieszka Zadura
Warsaw University of Life Sciences (SGGW),
Department of Environmental Improvement
Nowoursynowska Str. 166, 02-787 Warsaw

Received: 06.09.2016
Accepted: 13.11.2016