Dishwashing detergents and their effects on respiration inhibition of activated sludge

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Abstract. Nowadays, many households in the Czech Republic have a dishwasher. Their use releases the remnants of the dishwashing detergents used therein into the sewerage network. These substances affect the activity and also the lifetime of microorganisms in wastewater treatment plants (WWTP). Research is focused on respiration inhibition of microorganisms contained in activation sludge from WWTP and their affected by dishwashing detergents. In view of Regulation No 259/2012 of the European Parliament and of the Council concerning the limitation of the total phosphorus content of dishwashing detergents (into force on 1 January 2017), there have been significant changes in the structure of these detergents. The article describes the effect of selected dishwashing detergents on respiratory inhibition of activation sludge from a large municipal WWTP Ostrava and a small municipal WWTP Michálkovice. Both of these WWTPs are owned by OVK (Ostrava waterworks and sewerage). Subsequently, the research is focused on the comparison of obtained results. The highest variation in values were measured for sample 3, where the inhibition measured when testing a sludge from a large WWTP differed by up to 60% from that measured when testing a sludge from a small WWTP. The research also evaluates possible causes of respiration inhibition of microorganisms when testing specific sample solution.

1. Introduction
Research is focused on respiration inhibition of microorganisms contained in activation sludge from WWTP. These microorganisms are affected by dishwashing detergents. Wastewater treatment plants (abbreviated WWTP) are facilities used for waste water treatment to a level that enables their safe discharge into surface water [1]. The main objective of all conventional wastewater treatment plants is to remove organic substances that are contained in wastewater [2]. The removal of these substances enables the activation process taking place in the WWTP. It is a process of cultivation of microorganisms in non-sterile conditions [3, 4]. For research purposes, respiration was used to assess the impact on microorganisms contained in the activation sludge. Respiration, or biological oxidation, is the most important metabolic process of microorganism cells occurring in the activation sludge. Thanks to this process, aerobic and some anaerobic organisms gain the energy needed for their life cycles [5]. Respiration inhibition is a condition in which the metabolism of microorganisms is gradually impaired by a certain toxic substance. In this case, the inhibitory toxicant is selected dishwaser detergent samples.

The samples examined affect the activation sludge respiration. Activated sludge is called a mixed culture that was first grown in Manchester in 1913 by long-term aeration of urban sewage [3]. The composition of the activation sludge (both qualitative and quantitative) depends directly on the inflow of waste water to which the sludge was grown and on the technological parameters at which the sludge activation is carried out [6]. According to Regulation (EU) No 259/2012...
of the European Parliament and of the Council, dishwasher detergents with a total phosphorus content of not more than 0.3 grams per dose of product shall not be placed on the market. The restriction applies to all phosphorus compounds and came into effect on 1 January 2017. For this reason, there have been significant changes in the composition of dishwasher detergents in recent years.

2. Methods
Two very different wastewater treatment plants were chosen for research purposes. The first was the Central Waste Water Treatment Plant in Ostrava (CWWTP Ostrava). This WWTP provides 98.7% wastewater treatment from Ostrava and was designed for 638,850 PE (population equivalent). Sewage and industrial waste water are treated here by mechanical-biological treatment [7, 8]. The second treatment plant became Wastewater Treatment Plant Michálkovice. It was designed for 5,280 PE. Into this small wastewater flows only sewage water coming from residents of Michálkovice and residents of nearby Rychvald [7, 8]. Both selected treatment plants belong to OVAK. Measurements of respiration inhibition were performed on respirometer Strathtox from company Strathkelvin Instruments. The methodology for measuring respiration inhibition is available in the CSN EN ISO 8192 document as well as in the Strathtox instrument documentation. The method used evaluates the influence of the test sample on microorganisms in the activation sludge. In our case, the tested sample was dishwashing detergents. Evaluation is performed by measuring the respiration rate of solutions at five different concentrations under predefined conditions. These respiratory rates were compared with blank sample respiration. Six microcathode electrodes are used for measurement [9]. The actual measurement was preceded by the collection of activation sludge from the activation tanks of CWWTP Ostrava and WWTP Michálkovice. These samples were always taken just before the measurement to keep the sludge fresh and not to affect the measurement. Upon arrival at the laboratory, the sludge was connected to an external aerator and the instrument preparation and electrode calibration were performed as described in the Methodology for Determining Respiratory Inhibition of Activating Sludge [10]. Other solutions, namely synthetic sludge, were also required for measurement.

Respiratory inhibition was measured in solutions of 13 selected samples. Samples from different manufacturers were selected for comparison. Because of the variety, we select a more types of samples – tablets, loose powders and, of course, gels. Almost all monitored products come from the Czech market. Excluding the last sample (sample 13) that was imported from Australia.

The waste water consumption per wash cycle was set at 10 liters for the purposes of this research. The waste water was evaluated as medium hard. The dosage was used according to the manufacturer's instructions for medium hard water, i.e. 1 tablet for the preparation in the tablet form, 30 ml for liquid form (gels) and 30 g for powder form. After preparation of all the stock solutions and activation sludge, the measurement was performed. Dilution were performed according to the dilution table (refer with: Table 1). After setting all the values necessary for measuring and running the test, the activation sludge was pipetted into all the measuring flasks, electrodes were inserted and the test started.

| Measuring container | Sample dilution [%] | Detergent sample [ml] | Distilled water [ml] | Syntetic sludge | Activated sludge |
|---------------------|---------------------|-----------------------|----------------------|----------------|------------------|
| 1                   | 0                   | 0                     | 10                   | 2              | 8.50             |
| 2                   | 20                  | 2                     | 8                    | 2              | 8.50             |
| 3                   | 40                  | 4                     | 6                    | 2              | 8.50             |
| 4                   | 60                  | 6                     | 4                    | 2              | 8.50             |
| 5                   | 80                  | 8                     | 2                    | 2              | 8.50             |
| 6                   | 100                 | 10                    | 0                    | 2              | 8.50             |
3. Results

Respiratory rate and respiratory inhibition of microorganisms were gradually measured in all samples. The results were recorded in tables and graphs separately for each type of activation sludge. In some cases, there was a clear increase in disruption of the metabolism of microorganisms in the activation sludge and a corresponding sharp decrease in respiratory rate. In other samples, the disruption of the metabolism of microorganisms was only mild, associated with a gradual decrease in respiratory rate.

For better clarity, respiration inhibition values for all samples were marked separately for each activation sludge. The results of measurements of the respiratory rate were compared in two groups - for activation sludge from CWWTP Ostrava and for activation sludge from WWTP Michálkovice.

In the first graph (refer with: Figure 1) the measured results of impaired metabolism of microorganisms contained in the activation sludge taken from the CWWTP Ostrava are recorded. The graph clearly shows that the metabolism of microorganisms gradually decreased and thus the respiratory inhibition increased gradually. In all cases, the sample solutions were the most toxic at 100% solution concentration. At a 20% concentration of the solution, the inhibition of microorganisms was minimal (up to 10%), with the exception of two samples, samples number 9 and 7, which subsequently proved to be most toxic. Except for these two cases, 50% inhibition was not exceeded. Thus, for this sludge were the most toxic samples 9, 7 and 4, shown in red on the attached graph. The least toxic was the sample number 12, marked in green.

![Figure 1. Comparison of respiration inhibition of all samples – activated sludge from CWWTP Ostrava.](image)

The second graph (refer with: Figure 2) shows the results of disruption of the metabolism of microorganisms contained in the activation sludge from the WWTP Michálkovice. In this case, the metabolism of the microorganisms was impaired even at low concentrations of the sample solution. The only solution that did not exceed 10% at 100% solution concentration was sample No. 10. This sample was evaluated to be least toxic to the activation sludge and is shown in green on the graph. For this sludge, the most toxic samples 7, 4 and 9, respectively, were shown in red on the attached graph.
4. Discussions
When comparing the measurement results for the activation sludge from the CWWTP Ostrava and the sludge from the WWTP Michálkovice, the values were found to be very different. First, the measured values for individual activation sludge were compared. Subsequently, these results were compared with each other, each for the activation sludge from both treatment plants tested with the same sample of dishwasher detergent. When comparing these two graphs, it is clear that the microorganisms contained in the activation sludge collected at the CWWTP Ostrava are considerably more resistant. In this case, it is a large municipal wastewater treatment plant. Together with sewage water from homes and civic amenities are also flows wastewater industry. On the other hand, the microorganisms contained in the activation sludge collected at the WWTP Michálkovice are considerably less resistant. It is a small municipal wastewater treatment plant, where only municipal waste water from civic amenities flows. This treatment plant is not affected by the presence of more pollutants in the inflow. It has been found that none of the compositions with the lowest effect on the metabolism of microorganisms contains oxygen-based bleaching agents. From this we conclude that the presence of oxygen bleaching agents directly and negatively affects the metabolism of microorganisms contained in the activation sludge. This assessment was evaluated according to the manufacturer's composition on the product packaging. We consider the results of sample 13 very interesting. This sample is not sold in the Czech Republic, but was imported from Australia. Thanks to the results of the measurement of respiration inhibition it ranked among the worse average and did not meet the original expectations of its low harmfulness to microorganisms contained in the activation sludge. However, this may be influenced by more lenient legislative requirements and, to a lesser extent, by a much lower population through which dishwasher detergents could be produced.

5. Summary
The resulting evaluations were significantly different for individual samples. Respiration inhibition values were compared separately for activation sludge from WWTP Ostrava and separately for activation sludge of WWTP Michálkovice in solutions of all concentrations. Subsequently, the results for both activation sludges were compared with each other. The highest differences between respiratory inhibition values were measured for sample 3, sample 4 and sample 7. In these samples the inhibition of the metabolism of microorganisms measured during testing sludge from the Ostrava WWTP differed by 60% compared to the values measured in the activation sludge
from Michálkovice. The lowest difference was measured in sample 2, where respiratory inhibition in both sewage sludges ranged between 50 and 54%.

Of the investigated samples of dishwashing detergents, compositions with a high inhibition of the metabolism of microorganisms appear to be the most harmful. This was measured in sample 7, when testing the activation sludge from the WWTP Michálkovice. A total of three other (sample 4, sample 9 and sample 3) were exceeded at 85% inhibition when testing this sludge. However, in the latter sample the threshold was only slightly exceeded.

Samples Nos. 10, 11 and 12 were evaluated as the most suitable detergents with the least harmful effect on microorganisms in the activation sludge. For all of these detergents, the inhibition value of the 100% dishwasher detergent sample concentration was less than 17%. All three cases were gel samples. Samples 1 and 5, in which respiratory inhibition did not exceed 28%, were determined by relatively noxious agents.

Oxygen bleaching agents have not been reported by the manufacturer as part of the product for any of the gel compositions. This supported lower toxicity for the metabolism of microorganisms contained in activation sludge from wastewater treatment plants.

In an overall comparison of the results, the activation sludge from the WWTP Michálkovice was evaluated as “more sensitive” to disruption of microorganisms metabolism. The fact that the activation sludge from the WWTP Ostrava is more resistant is most likely influenced by the presence of industrial waste water in the treated water.

In conclusion, the metabolism of microorganisms in sludge is largely influenced by the overall composition of dishwasher detergents. However, the composition of wastewater at the inflow to the WWTP also plays a very important role. In sewage plants, which are supplied not only with waste water from public facilities, but also with industrial water, the microorganisms contained in the sewage sludge are much more resistant to possible disruption.

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References

[1] Waste water disposal up to 2,000 population equivalent: Methodical manual 2009 (Prague: Ministry of the Environment of the Czech Republic) (in Czech)
[2] Waste water treatment (online) (Prague: Czech Technical University- Faculty of Civil Engineering)
[3] Dohányos M, Koller J and Strnadová N 2004 Waste water treatment (Prague: Publishing house of the Institute of Chemical Technology in Prague) (in Czech)
[4] Seviour R and Nielsen P H 2010 Microbial Ecology of Activated Sludge (London: IWA Publishing)
[5] Davies P S 2005 The biological basis of waterwaster treatment (Glasgow: Strathkelvin Instruments Ltd) pp 3-11
[6] Hlavínek P, Mičín J and Prax P 2003 Sewerage and wastewater treatment: Waste water treatment (Brno: Technical University Brno – Faculty of Civil Engineering) (in Czech)
[7] Wastewater treatment plant 2017 (Ostrava: Ostrava waterworks and sewerage) (company materials Ostrava waterworks and sewerage – OVAK) (in Czech)
[8] Wastewater treatment plant. Ostrava waterworks and sewerage – OVAK 2017 (online) (Ostrava: Ostrava waterworks and sewerage – OVAK)
[9] Škrobánková H and Škrobánková S 2011 Methodology for determination of short-term biological oxygen demand (Ostrava: VŠB – Technical University of Ostrava, Faculty of Mining and Geology) (in Czech)
[10] Škrobánková H and Škrobánková S 2011 Methodology for determination of respiration inhibition of activated sludge (Ostrava: VŠB – Technical University of Ostrava, Faculty of Mining and Geology) (in Czech)