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BIODEGRADABILITY STUDIES OF KOHTLA-JÄRVE WASTEWATERS BY ACTIVATED SLUDGE RESPIRATION

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The activated sludge respiration measurement is proposed for assessing the activated sludge processes and biological treatability of wastewaters. Different municipal and industrial wastewaters influents to the Kohtla-Järve wastewater treatment plant were analysed and compared on the basis of exogenous oxygen uptake rates of activated sludge. The kinetic parameters of biodegradation processes were determined by monitoring the degradation-associated oxygen consumption in tests with different amounts of wastewaters and simple biokinetic model of activated sludge respiration.

Introduction

Activated sludge wastewater treatment plants usually receive wastewater with varying flow rate and waste concentration. A sufficient degree of wastewater purification needs controlling. By measuring the influent waste concentration, useful information for control can be obtained. However, the measures like biochemical oxygen demand (BOD), chemical oxygen demand (COD), total organic carbon (TOC), used to express the waste concentrations, are often insufficient for checking purposes in process operation. There is also a need to predict how the activated sludge in treatment plant would respond to changes in wastewater composition and concentrations.

In recent years efforts have been made to develop respirometric techniques for the continuous as well as batch measurements of activated sludge processes for monitoring purposes in treatment plants. Methods based on a respirometric principle have been proposed to determine short-term biological oxygen demand [1] and readily biodegradable organic matter [2], toxicity [3] and biokinetic parameters of non-toxic as well as toxic wastewaters [4-6].

The aim of this study is to develop a method for the estimation of the degradability of wastewater in the processes involving activated sludge itself. The implementation of oxygen concentration measurements is proposed and tested to receive biodegradability information on the basis of oxygen uptake rates of activated sludge and a biokinetic model.

The proposed method based on the oxygen consumption measurement of activated sludge can also be used for the investigation of sludge characteristics and evaluation of the impact of wastewater influent to activated sludge processes.

Materials and Methods

The activated sludge was obtained from the second-step aeration basin of the regional wastewater treatment plant of RAS "Kiviter", Kohtla-Järve, Estonia. The sludge samples studied were taken from the same aeration basin. All the results obtained on the sludge are based on activated sludge taken from the same place simultaneously.

The wastewaters studied were different influents, both municipal and industrial, to the above-mentioned treatment plant. The specific substrate used for the measurement of the heterotrophic respiration rate of different activated sludge samples was phenol. It was chosen because phenol is one of the components in industrial wastewaters of the oil shale processing industry flowing to the treatment plant. Phenol gave good results without any need for the adaptation of sludge.

Experimental

All tests were performed at temperature of 22 ± 1 °C. The experimental set-up consisted of an open flask filled with 1 liter of activated sludge. First of all, the activated sludge was aerated. The aeration was stopped and the endogenous respiration of the sludge was measured. Then a pulse of substrate or wastewater was injected. As a result of the substrate/wastewater addition, the activated sludge showed an increased oxygen uptake rate, the so-called exogenous respiration which caused a considerable decrease in dissolved oxygen content in the test media. Since there was no continuous aeration in the test flask, the dissolved oxygen level decreased until it reached almost zero.

An oxygen meter (BODetector, AMS, Estonia) was used to measure the oxygen concentration in the tests. Measured data were recorded every 2 seconds by a computer, from which the oxygen uptake rates (*OUR*) were calculated and further analysed.

Basic Assumptions and Concept Development

The oxygen uptake rate curve reflects the kinetics of aerobic biodegradation of substrates by the activated sludge. Two aerobic processes can be involved, i.e. nitrification and carbon source oxidation. These processes are independent and their oxygen uptake rates add up.

In this study, only the aerobic degradation processes of C-substrates by heterotrophes are investigated. Oxygen consumption associated with nitrification is not included in the model.

The decrease in dissolved oxygen concentration in the investigated media is determined by microbial oxygen uptake for endogenous and exogenous respiration:

$$\frac{dc_{O_2}}{dt} = - OUR_{end} - OUR_{ex} = - OUR_{tot} \tag{1}$$

Typical oxygen profile resulting from an endogenous respiration and the addition of substrate is shown in Fig. 1*a*.

The oxygen uptake rate can easily be calculated from the data by measuring temporal oxygen concentration changes in the test system:

$$OUR = \frac{dc_{O_2}}{dt} = \frac{c_1 - c_2}{t_2 - t_1} \tag{2}$$

The plotting of calculated *OUR* values against time results in a profile shown in Fig. 1*b*. In test assay the substrate concentration is continuously changing, the reaction rate decreases with a decrease in substrate concentration and hence the oxygen uptake rate also decreases along time.

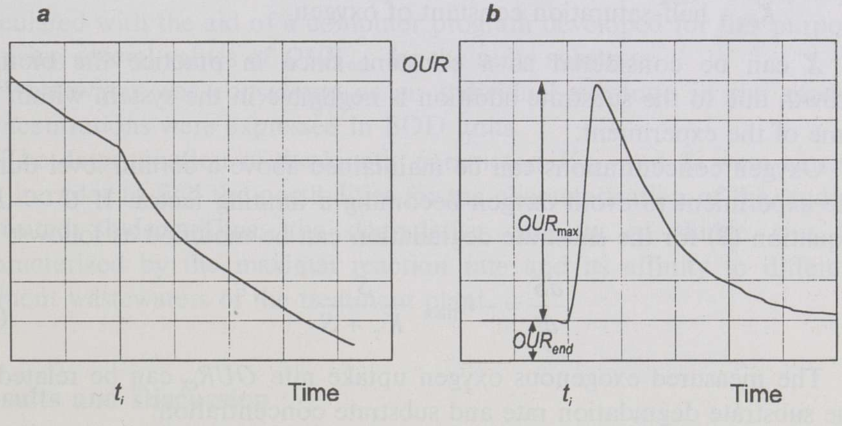

Fig. 1. Schematic representation (*a*) of the decrease of oxygen concentration in the test and (*b*) of the oxygen uptake rate profile

The kinetics of oxygen uptake in substrate degradation processes by activated sludge at a constant temperature depends on three important factors: the concentration of dissolved oxygen, biomass concentration and substrate concentration in test media. For the description of the degradation of substrate by activated sludge it is rather convenient to use a formulation based on analogy with saturation kinetics in monomolecular adsorption. This model suggests that the dependence of reaction rate on substrate concentration can be described by two constants, namely by maximum rate and limitation constant. Most biochemical reactions according to the Monod or Michaelis-Menten kinetics have been actually modelled by using the above-mentioned saturation kinetics. According to these models, at high substrate concentration the reaction rate is of zero order and proceeds at maximum velocity while at low substrate concentration the rate becomes first order and concentration-dependent.

The rate equation describing the degradation process of an individual substrate by activated sludge can be based on the kinetics for oxygen and the substrate as a rate limiting factor at a constant biomass concentration. It can be expressed by the following equation:

$$\frac{dS}{dt} = -V_{\max}\left(\frac{S}{K_s + S}\right)\left(\frac{C}{K_{ox} + C}\right) \tag{3}$$

where $V_{max} = k X$

V_{max} - maximum substrate consumption rate
X - concentration of active biomass
k - rate constant of the limiting step
S - concentration of substrate
C - concentration of oxygen
K_s - half-saturation constant of substrate
K_{ox} - half-saturation constant of oxygen

X can be considered as a constant since in practice the biomass growth due to the substrate addition is negligible in the system within the time of the experiment.

Oxygen concentrations can be maintained above a certain level during the experiment to avoid oxygen becoming a limiting factor. If $C >> K_{ox}$, Equation (3) for the substrate degradation can be modified as follows:

$$\frac{dS}{dt} = -V_{\max}\frac{S}{K_s + S} \tag{4}$$

The measured exogenous oxygen uptake rate OUR_{ex} can be related to the substrate degradation rate and substrate concentration:

$$OUR_{ex} = -\nu\frac{dS}{dt} \tag{5}$$

where v - coefficient accounting for the quantity of oxygen that has been consumed per unit of substrate in the degradation process.

The temporal dependence of the exogenous oxygen uptake rate $OUR_{ex}(t)$ can be calculated by subtracting OUR_{end} from OUR_{tot}:

$$OUR_{ex}(t) = OUR_{tot}(t) - OUR_{end} \tag{6}$$

OUR_{end} was calculated from the respirogram for the range $t < t_i$ where $OUR_{tot} = OUR_{end}$ (Fig. 1*b*). The endogenous respiration rate can be assumed constant for the time interval of one test and therefore can easily be eliminated from the total respiration process.

For the range $t \geq t_i$ the maximum oxygen uptake rate OUR_{max} was determined at a constant biomass concentration for a certain amount of added substrate (Fig. 1*b*).

$$OUR_{tot}(t_i) = OUR_{end} + OUR_{max} \tag{7}$$

Several values of OUR_{max} can be found by adding different known quantities of the substrate to the activated sludge. Further, the dependence of the values of OUR_{max} on the substrate concentration was investigated.

With the aid of Equations (4) and (5), OUR_{max} can be related to the substrate concentrations. Thus,

$$OUR_{max_1} = vV_{max}\frac{S_1}{K_s + S_1} \tag{8}$$

$$OUR_{max_2} = vV_{max}\frac{S_2}{K_s + S_2} \tag{9}$$

In principle, values of the V_{max} and K_s can be analytically determined from the Equations (8) and (9). In the present study V_{max} and K_s were calculated with the aid of a computer program developed for this purpose by using several values of OUR_{max} for the same substrate.

Wastewater was considered as an individual substrate in the model. Concentrations were expressed in BOD units.

The determination of the kinetic parameters V_{max} and K_s were carried out in order to find the possibilities for the characterization of the studied activated sludge. Thus, the degradative capacity of sludge can be characterized by the maximal reaction rate and its affinity to different influent wastewaters of the treatment plant.

Results and Discussion

Before the sampling place for taking sludge for wastewater experiments was chosen, the sludge samples from different parts of the aeration basin were taken and tested to phenol. Schematic representation of the sampling sites and their oxygen contents is given in Fig. 2.

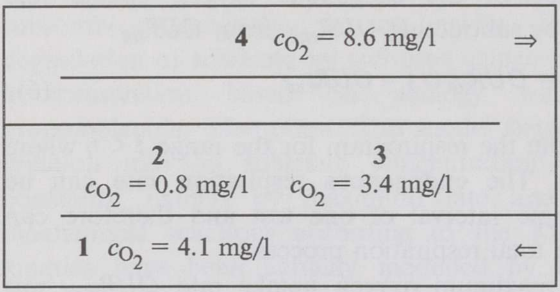

Fig. 2. Schematic representation of the sludge sampling sites in the aeration basin. The dissolved oxygen concentrations, representative of the sites, are shown

Table 1. **Comparison of Kinetic Parameters of Phenol Degradation for Different Sludge Samples**

Sludge	V_{max}, mg/l min	K_s, mg/l
1	0.58	0.41
3	0.53	0.39
4	0.57	0.52

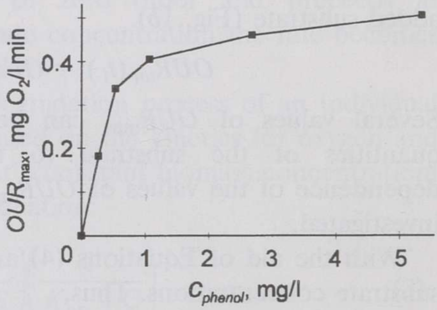

Fig. 3. OUR_{max} as a function of added phenol concentrations for sludge 3

Sludge *3* was chosen for further studies because it showed better reproducibility of the endogenous oxygen uptake rate than the other samples tested. In Fig. 3 the relationship between the OUR_{max} values and added phenol concentrations is illustrated. Table 1 includes kinetic parameters of phenol degradation for different sludge samples.

The studied influents to the Kohtla-Järve municipal wastewater treatment plant are listed and characterized in Table 2.

Table 2. **Studied Influent Wastewaters to the Kohtla-Järve Wastewater Treatment Plant**

Wastewater	BOD_7, mg/l	COD, mg/l
1. Municipal from Kohtla-Nõmme	105	363
2. Municipal from Kohtla-Järve	145	419
3. From Velsicol Eesti AS	279	320
4. From Kiviter tar removal	380	930
5. After equalization basin	408	856
6. From Kiviõli	820	1860
7. Leaching from ash heaps	940	1860
8. From Kiviter dephenolization	2160	4370
9. Mixed from Püssi	2550	5670
10. Industrial from Püssi	3920	8740

The typical recorded decrease of oxygen concentration and the oxygen uptake rate profile of the experiment are presented in Figures 4 and 5, respectively.

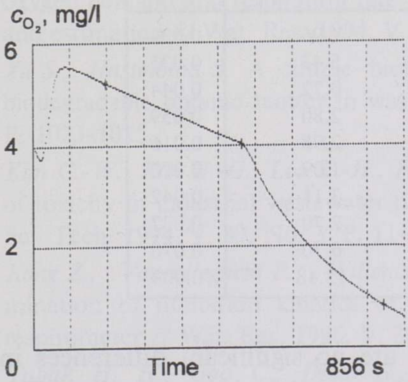

Fig. 4. Oxygen concentration profile resulting from the addition of 1 ml wastewater (8) from the Kiviter dephenolization plant to the activated sludge

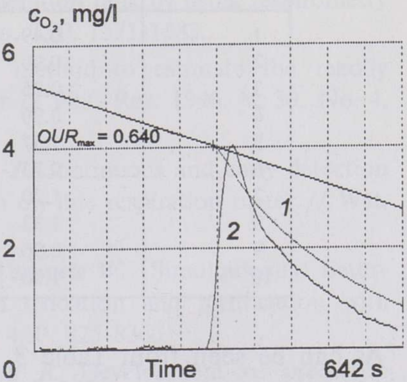

Fig. 5. Measured oxygen concentrations (curve *1*) and calculated respiration rates (curve *2*) in case of the addition of 1 ml wastewater (*8*) from the Kiviter dephenolization plant

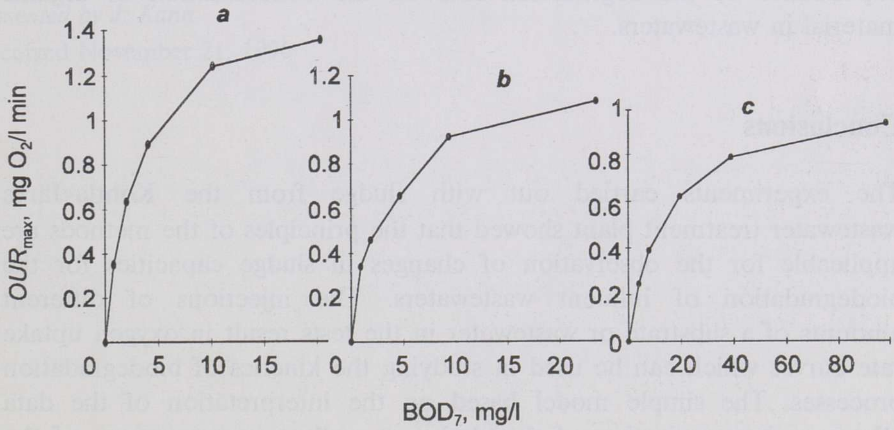

Fig. 6. OUR_{max} as a function of added BOD concentrations: (*a*) wastewater sample (*5*) taken after the equalization basin in the treatment plant, (*b*) leachate from oil-shale ash heaps (*7*) and (*c*) industrial wastewater from Püssi (*10*) were used as a substrate

In Fig. 6 the dependences of the OUR_{max} values on the concentration of different wastewaters in BOD units are shown.

The kinetic parameters V_{max} and K_s of the biodegradation of wastewaters calculated on the basis of the model introduced above (Equations (8) and (9)) are given in Table 3.

Table 3. **Estimated Kinetic Parameters V_{max} and K_s and the Sum of Squared Errors δ for the Dependences**

Wastewater	V_{max}, mg/l min	K_s, mg BOD_7/l	δ
1	0.49	1.96	0.034
2	0.90	5.43	0.031
3	0.75	0.72	0.044
4	0.99	2.80	0.059
5	1.57	2.98	0.016
6	0.73	1.09	0.020
7	1.20	3.11	0.042
8	1.33	2.70	0.037
9	0.96	6.70	0.070
10	1.06	13.48	0.004

As can be seen from Table 3, there are no significant differences in the kinetic parameters of industrial and municipal wastewaters. The applied approach shows similar V_{max} values for the tested wastewaters. However, the degradation rate for the Kohtla-Järve municipal wastewater was considerably lower than that for other studied wastewaters. The highest degradation rate was achieved for the wastewater taken after the equalization basin. The introduced affinity constants K_s express the dependence of the degradation rate on the concentration of organic material in wastewaters.

Conclusions

The experiments carried out with sludge from the Kohtla-Järve wastewater treatment plant showed that the principles of the methods are applicable for the observation of changes in sludge capacities for the biodegradation of influent wastewaters. The injections of different amounts of a substrate or wastewater in the tests result in oxygen uptake rate curves which can be used in studying the kinetics of biodegradation processes. The simple model based on the interpretation of the data allows a characterization of the sludge as well as a comparison of the biodegradability of different influents.

However, the current approach is only a beginning and its application should be specified in further studies.

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