XVIII IMEKO WORLD CONGRESS
Metrology for a Sustainable Development
September, 17 – 22, 2006, Rio de Janeiro, Brazil

COMPLEX BIOLOGICAL DEGRADABILITY TEST OF PHARMACEUTICAL WASTEWATERS

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Abstract: The composition and, consequently, the biological degradability (BD), of pharmaceutical wastewaters are not constant in time. To optimize the wastewater management of a pharmaceutical factory, real time data are needed about the BD of wastewaters. In our experiments, it was found that measurements using a lab-scale wastewater treatment plant (LWWTP) and a short-time BOD (RBOD) meter, as well as the combined evaluation of RBOD and COD data ensured rapid and accurate assessment of BD of wastewaters.

Keywords: wastewater, biological degradability, zeolite

1. INTRODUCTION

Biological degradability (BD) is one of the most critical quality parameters of wastewaters. BD has a determinant role not only in the selection of wastewater treatment technology to be applied, but in the determination of expected effluent quality, as well. There is a wide range of BD of organic matters found in pharmaceutical wastewaters. In general terms the following can be said:

- Organic matters of high molecular weight are more difficult to oxidize biologically than those of less molecular weight.
- In the case of high concentrations of organic and inorganic compounds the process of biological oxidation is slower than in the case of low concentrations.
- Aliphatic hydrocarbons are easier to decompose than unsaturated ones.
- Substituted and additional groups reduce the speed of biological oxidation.
- Organic matters containing triple bound carbon atom(s) cannot be oxidized biologically.
- Appropriate BOD_5/N/P ratio is a prerequisite of efficient decomposition. For communal wastewaters its optimum is 150/5/1 [1].

Biological degradability is usually determined by the standard BOD_5 method [2] which, having a five-day time demand, is unsuitable for controlling the wastewater treatment technology. The instruments used for respirometric measurement [3, 4] are not capable of modeling the operation of the biological stage of wastewater treatment plants (WWTP).

To solve the problem equipment for (1) modeling the operation of biological WWTPs, (2) measuring short-time BOD (RBOD) were developed and used for forecasting BD of wastewaters.

2. INSTRUMENTATION, METHODS OF ANALYSIS

2.1 Lab-scale wastewater treatment plant

Innovative equipment also capable for respirometric measurements was used for modeling the operation of biological WWTPs having an aeration basin and a secondary clarifier [4. The operation of equipment was based on conducting oxygen in a closed system at constant pressure through the wastewater examined. Oxygen consumed by the biological system was continuously measured so that an oxygen flow equivalent to that consumed was electrochemically generated. Carbon dioxide produced by the biological system was bound in an alkaline gas washer. The lab-scale wastewater treatment plant (LWWTP) and its schematic diagram is shown in Photo 1 and Fig. 1.

Photo 1 Picture of lab-scale wastewater treatment plant

The parameters of experiments (flow rate, hydraulic detention time, biological load, sludge concentration, recirculation rate, excess sludge removal) set on the LWWTP were calculated on the basis of the operational data of the WWTP of North Budapest. A description of continuous laboratory experiment is as follows: 2,000 ml wastewater was poured into the biological reactor of the LWWTP. The reactor was continuously aerated and fed with raw wastewater. The feeding rate of raw wastewater and the rate of recirculation were set to 3,200 ml/day (15-hour detention time) and 100 %, respectively. After the start-up period of 24-hour, the sludge removal was set to 1 g/day and the oxygen uptake, as well as the quality parameters of effluent water were determined. The experiments were carried out at detention times ranging from 5 to 48 hours with and without modified zeolite (MZ) additive. The goal of MZ application was to accelerate the process of biological decomposition. A grain size of MZ was between 10 - 110 μm and its quantity related to sludge concentration was 15 %.

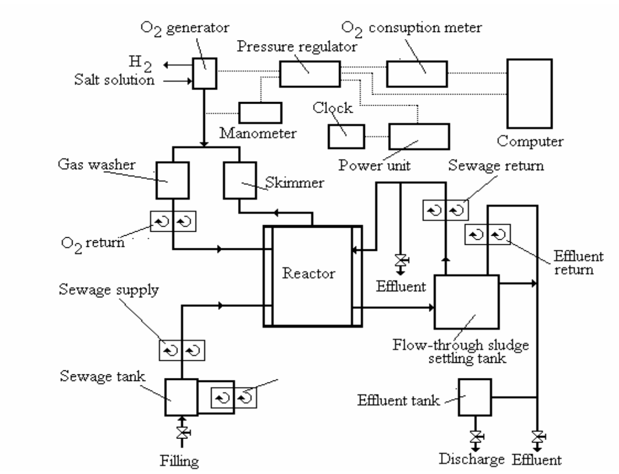

Fig. 1 Lab-scale wastewater treatment plant

2.2 RBOD measurement and RBOD/COD ratio

A respirometer of open system as shown in Fig. 2 was used for the determination of RBOD. The operation of the equipment was based on conducting air into the suspension of wastewater and activated sludge samples. The concentration of dissolved oxygen (DO) in the suspension was measured with an amperometric oxygen probe (WTW GmbH, Germany, type: Stirr OxG).

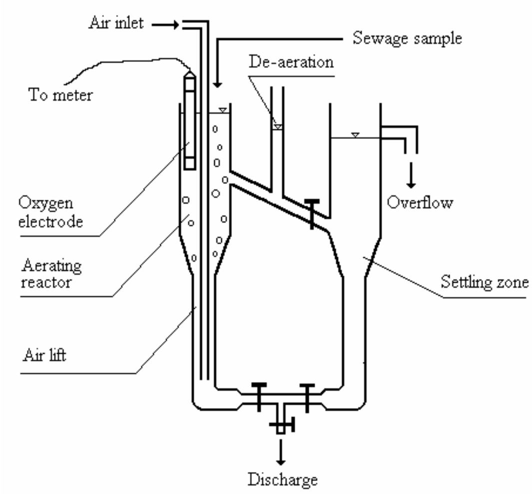

Fig. 2 Discontinuous RBOD Meter Schematic diagram

For measuring RBOD, substrate respiration was integrated according to time. The RBOD value of the wastewater to be tested was proportional to the space below the respiration curve. To calculate RBOD, a known quantity of V_k was injected from a known $RBOD_k$ calibrating solution (Na-acetate) into the reactor, at which time the space below peak F_k was recorded. A wastewater flow of V_{sz} was metered in the reactor and the territory below peak F_{sz} shaping in the course of decomposition was determined. Based on the foregoing, RBOD was calculated according to equation:

$$RBOD = RBOD_k \frac{V_k F_{sz}}{V_{sz} F_k} \quad (1)$$

A description of RBOD experiment is as follows: Equipment filled with activated sludge (2,500 ml) was continuously aerated (2.5 L/min). When the DO concentration in the suspension became constant in time (increased up to 10 mg/L) 25 – 250 ml wastewater was poured into the biological reactor of respirometer. According to the effect of the biodegradable constituents of wastewater, the DO concentration in the suspension dropped down, then increased again. When the DO concentration increased up to its original value the entire process of measurement was repeated, however 25 - 250 ml CH_3CCONa solution of 5 g/L was added to the activated sludge instead of wastewater.

The experiments were carried out with and without MZ additive. A grain size of MZ was between 10 - 110 μm and its quantity related to sludge concentration was 15 %.

A typical respiration curve developed in the course of RBOD measurement is shown in Fig. 3. On the basis of RBOD results, the RBOD/COD ratio was calculated which gave an idea as to BD of the effluent. RBOD/COD higher than 0.5 generally indicates efficient BD, while a value lower than 0.05 indicates that the effluent is practically non-degradable. Interim values indicate partial decomposition.

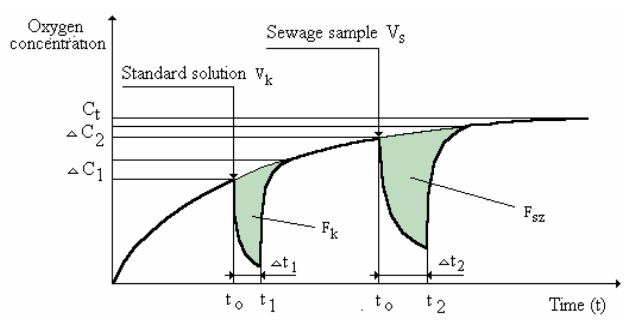

Fig. 3 Typical respiration curve of RBOD measurement

2.3 Continuous anaerobic analysis

A continuous lab-scale digester of which schematic diagram is illustrated on Fig. 4 was used to accomplish anaerobic tests.

A description of anaerobic experiments is as follows: The anaerobic equipment was filled with 24 L wastewater containing anaerobic activated sludge in 4.0 g/L concentration. The feeding rate of raw wastewater and the rate of recirculation were 6 L/day (4-day detention time) and 100 %, respectively. After the start-up period of 24-hour, the sludge removal was set to 6 g/day and the quality parameters of effluent, as well as the volume of biogas generated were determined. Temperature of the anaerobic reactor was kept on 35 ^oC. Anaerobic sludge used to the experiments originated from the WWTP of Veresegyház.

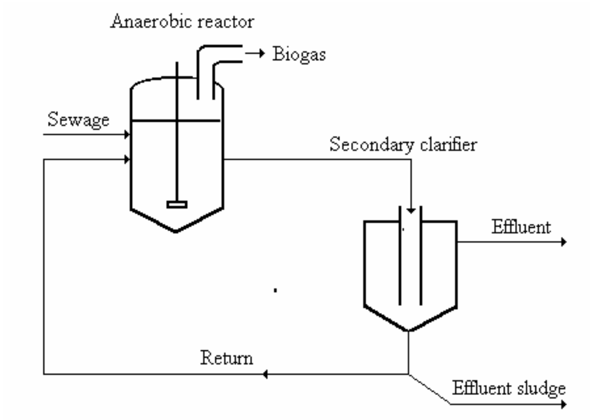

Fig. 4 Schematic diagram of continuous lab-scale digester

3. RESULTS AND DISCUSSION

3.1 Characterization of wastewaters

Averaged wastewater and veratryc aldehyde, as well as decyanidation mother lye of a large Hungarian pharmaceutical factory were analyzed for biochemical degradability. Ensued from the production of synthetic pharmaceuticals, the wastewaters contained high concentrations of alcoholics and acetic acid, toluene, xylene and other benzene products, as well as chlorinated hydrocarbons (chloro-benzene, dichloroethane, benzene-chloride). Moreover, all of the effluent contained butyric acid, formaldehyde, dimethyl amine, dimethyl formanide, sodium tartrate, sulfanilic acid, dimethyl sulphate, ammonium salts, other inorganic salts, acids and alkalis.

3.2 Examination of traditional parameters

The measurement of traditional components, namely COD, BOD_5, NH_4-N, total-P, total salts, suspended solids, organic solvent extract characterizing the composition of wastewaters were accomplished according to the Standard Methods [5]. Water quality parameters of the wastewaters are summarized in Table 1.

Table 1 Data of wastewater analysis

Water quality parameter	Type of wastewater		
	Averaged	Veratryc aldehyde mother lye	Decyanidation mother-lye
pH	7.0	13.1	9.6
COD (mg/L)	4,900	212,060	40,568
BOD_5 (mg/L)	2,890	68,492	4,770
BOD_5/COD ratio	0.59	0.33	0.12
Organic nitrogen, (mg/L)	10.3	56	1,512
Total-P, (mg/L)	3.4	10.5	10.6
NH_4_N (mg/L)	116	110	375
NO_3- N (mg/L)	10.0	5.2	6.1
CCl_4 extract (mg/L)	51	18	12
Total salt (g/L)	6.2	183	99

3.2.1 Quality of averaged wastewater

Concentrations of COD, BOD_5, total salts and ammonia, which characterize the extent of contamination, were relatively high. However, organic nitrogen and phosphorus concentrations were remarkably low. The average proportion of COD/BOD_5/N/P was found to 1,441/850/40/1.

Since the phosphorus content of the raw wastewater was too low to an effective biological decomposition, the phosphorus concentration in the wastewater was increased up to 20 mg/L by adding K_2HPO_4. Accordingly, the average nutrient proportion was modified to be 176/103/5/1 in the wastewater.

The BOD_5/COD ratio had a relatively high value. It meant that the organic compounds of the wastewater were easily degradable.

3.2.2 Quality of mother-lye

Both types of mother-lye featured extremely high COD values; 212 g/l for the veratryc aldehyde and 40 g/l for the decyanidation. The BOD_5 values and the rates of BOD_5/COD were low particularly in the case of decyanidation mother-lye indicating its toxicity.

The phosphorus concentration was rather low in both mother-lye, therefore additional phosphorous source (K_2HPO_4. solution) was needed to make the biological treatment possible.

The salt concentration of both mother-lye was extremely high. The direct biological treatment of aqueous solutions of high salt concentration is generally due to toxicity of salts doubtful even in the case of optimal organic concentration. Consequently diluted samples were used for the biodegradability tests.

3.3 Experiments using LWWTP

In order to determine the extent of BD and the optimal time of treatment, the relationship between effluent COD of LWWTP and detention time (time of treatment) was investigated. (COD decrease is directly proportional to BD.)

3.3.1 Averaged wastewater

The COD of treated wastewater as a function of detention times are shown in Fig. 5. A low treatment efficiency, 38 %, was evident after 10 hours of detention. Nevertheless, decomposition of organic substances improved with detention time. The relationship between the COD of effluent and the detention time showed a “run-off to optimum” curve. The curve minimum gives the attainable residual COD value. The residual COD minimum was obtained by a 24-hour detention time. In Fig. 6, a load of 0.53 $kg_{COD}kg^{-1}day^{-1}$ is shown to belong to a 24-hour detention time. Given a strong wastewater of complex composition to degrade, the minimum CODs of 817 mg/L (without MZ additive) and 590 mg/L (with MZ additive) are acceptable.

The influence of MZ additive on decomposition of organic compounds was examined at detention times of 15, 20, 24 and 36 hours. The quality of effluent improved by 25 – 30 % due to the effect of MZ.

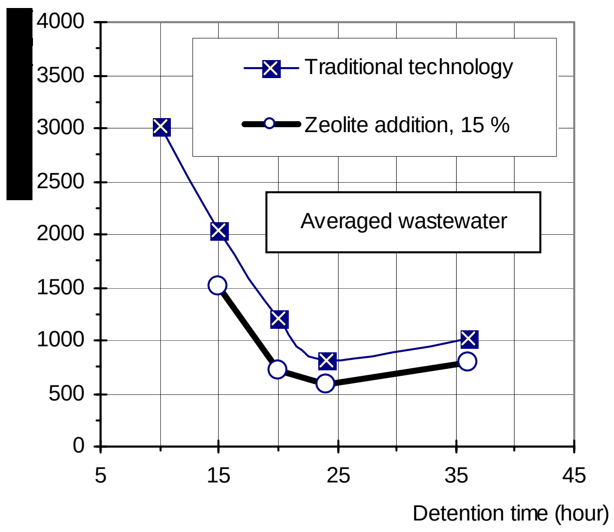

Fig. 5 Relationship between effluent COD and detention time (Measurements using LWWTP)

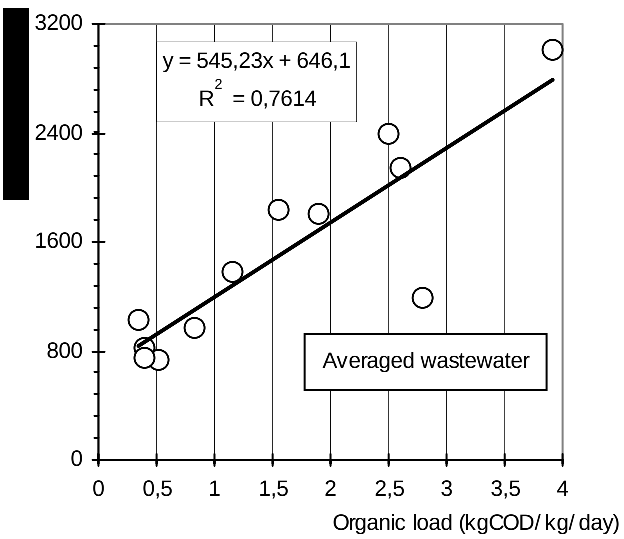

Fig. 6 Effluent COD concentration as a function of organic load (Measurements using LWWTP)

Fig. 7 shows specific oxygen consumption of the activated sludge system as a function of COD load. It is seen that an increase in load, over 0.53 $kg_{COD}kg^{-1}day^{-1}$, led to a substantial increase in oxygen consumption. A change to the opposite of oxygen consumption was observed for lower loads (0.34 $kg_{COD}kg^{-1}day^{-1}$) that could be explained by sludge decomposition and increasing endogenous sludge respiration.

Activated sludge ensued from biological treatment settled well at each time of detention and no any formation of filaments or scum was observed. Index Mohlmann characterizing the settling of sludge ranged from 80 ml/g to 110 ml/g.

3.3.2 Mother-lye

Activated sludge treatment of veratryc aldehyde mother-lye took place with the addition of communal wastewater. 1 litre of mother-lye was diluted with 29 litre of communal wastewater. A 5-hour detention time yielded a treatment efficiency of merely 8 %. The decomposition efficiency improved with detention time, however the maximum value of decomposition rate remained at 41 %, even at 48 hours of detention. This value, in the practice of biological treatment, is considered poor.

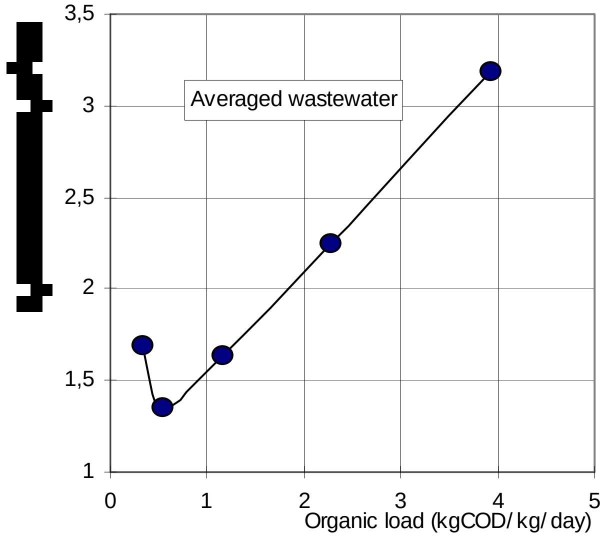

Fig. 7 Relationship between oxygen consumption and organic load (Measurements using LWWTP)

Similarly to the mother-lye of veratryc aldehyde, the activated sludge treatment of decyanidation mother-lye took place with addition of communal wastewater. Volumetric mixing ratio of communal wastewater and mother-lye was 8:1. Efficiency of the COD decomposition was only 33 % even for the longest, 48-hour detention time. Results ascertained uneconomical biological treatment of decyanidation mother-lye even if that was mixed with communal wastewater.

The relationship between the COD concentration of treated mother-lye and detention time is illustrated on Fig. 8.

Based on the results of continuous activated sludge treatment the followings can be stated:

- Both mother-lye, although ensued elsewhere, behaved nearly the same
- Both mother-lye were hard to decompose biologically
- Even under 48-hour time of treatment (top limit of possible technological conditions), poor decomposition efficiency was attained.

Based on the foregoing it was concluded that none of the mother-lye could economically be treated by activated sludge technology, even if the lye were mixed with communal sewage.

3.4 RBOD measurements

The RBOD data of respirometric experiments and the data of BOD_5 measurements, as well as the ratios of RBOD/COD and BOD_5/COD are summarized in Table 2. Data show that RBOD, like BOD_5, suits for describing the biological degradability of wastewaters. RBOD measurements however, resulted in lower values than BOD_5. It can be explained by the different time of treatment pertaining to the RBOD and BOD_5 methods. Organic compounds hard to decompose need longer biological treatment. Taking into consideration that the time demand of an RBOD measurement is only 1- 2 hours, it is easy to understand that BOD_5 values exceed RBOD ones, in spite of the significantly better DO supply of the samples measured for RBOD.

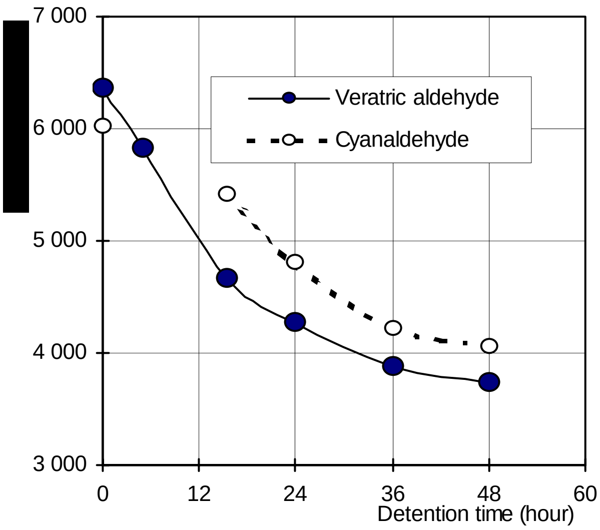

Fig. 8 Relationship between effluent COD concentration and time of treatment (Measurements using LWWTP)

Table 2 Data of RBOD and BOD_5 measurements

Water quality parameter	Type of effluent					
	Averaged		Veratryc aldehyde mother lye		Decyanidation mother-lye	
RBOD (mg/L)	2,415	2,785*	55,212	66,758*	3,490	3,996*
BOD_5 (mg/L)	2,890	3,104*	68,492	80,422*	4,770	5,206*
RBOD/COD ratio	0.49	0.57*	0.26	0.32*	0.09	0.10*
BOD_5/COD ratio	0.59	0.63*	0.33	0.38*	0.12	0.13*
$(BOD_5–RBOD) / BOD_5$	16 %	10* %	19 %	17* %	27 %	23* %

Legend: *Data pertaining to experiments using MZ additive

3.5 Anaerobic biological degradability

Based on the results of the treatment of averaged wastewater the following can be said:

- Wastewater was anaerobically degradable, balance in the anaerobic system, however was maintainable only for low loads (1 $kg_{COD}day^{-1}$; t = 4 days).
- Low rate in gas generation (0.1 dm^3/g_{COD}) and low speed of decomposition did not permit any high-load system (8 - 10 $kg_{COD}m^{-3}day^{-1}$) to operate. It meant that anaerobic treatment was uneconomical.
- Residual COD values attainable by aerobic and anaerobic processes were practically the same (817 and 843 mg/L). It leads to conclude that presumably the same constituents of wastewater permit decomposition by aerobic and anaerobic biological processes.

Based on the results of the digestion of mother-lye it can be stated that:

- for both mother-lye, at 48-hour detention time, the anaerobic treatment resulted in nearly the same decomposition efficiency (veratryc aldehyde: 43 %, cyanaldehyde: 38 %) as the aerobic one (veratryc aldehyde: 41 %, cyanaldehyde 33 %).
- the extent of mother-lye decomposition might be increased by two-stage mesophilic and single-stage thermophilic anaerobic processes [6], however a decomposition efficiency of 80 – 85 % (at t = 48 hours) approved as an economic efficiency index could not be accounted for.

3.6 Effect of modified zeolite on biological degradability

Data of Table 2 show that application of modified zeolite improved the biological degradability of every wastewater. The percentage value of degradability increase ranged between 10 - 24 % expressed in RBODCOD and between 1 – 15 % expressed in BOD_5/COD. It means that MZ additive was more effective in the case of organic compounds easy to decompose.

4. CONCLUTIONS

The measurements accomplished using a LWWTP and a short-time BOD meter, as well as the mutual assessment of RBOD and COD data ensure fast and reliable information on biological degradability of wastewaters.

The averaged pharmaceutical wastewater tested permits the activated sludge treatment. The mother-lye cannot successfully be treated by biological methods. Because of high toxic effect and residual COD, mother-lye impairs the decomposition efficiency of other wastewaters ready to decompose. Mother-lye therefore, should be abstracted from the biological wastewater treatment.

The anaerobic treatment of all the types of wastewaters yields nearly same effluent quality as the aerobic one.

Modified zeolite additive enhances the aerobic decomposition of organic constituents, therefore its application to wastewater treatment is recommended.

ACKNOWLEDGMENTS

The NATO Science for Peace Programme jointly supported this research along with the Hungarian Ministries of Education, Economy and Transportation and the National Office for Research and Technology in Hungary.

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