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TOXICITY OF MERCURY IN BIOLOGICAL SEWAGE TREATMENT ON SPRINKLING BEDS

Toxicity of mercury was studied in biological aerobic filters while treating synthetic wastewater. Experiments were done on bench-scale. Influent was a reproducible water solution with constant organic content. After starting period mercury was added in gradually increasing concentrations. TOD, BOD, COD, and permanganate values showed a 40–60% reduction of ogranic matter when mercury content in the feed solution did not exceed 400 μg/dm^3. Shock load of mercury was also used to test the adaptation of microorganisms. The biomass was observed microscopically. In the course of the experiment there are observed the changes concerning chiefly protozoan species and the higher microorganisms.

1. INTRODUCTION

Mercury and its compounds are well known as dangerous contaminants of the environment. Unfortunately, human life is closely connected with that toxic element. In spite of the efforts to shorten the number of mercury applications, man is compelled to use mercury in many fields. The uses distinguished as the dissipative ones [10] (paints, agriculture, pharmaceuticals, plastics, etc) still cause significant, irreversible discharge of mercury into the environment. The technologies known as potentially recyclable also give a serious emission of mercury regardless the introduction of new systems for removal and recovery of mercury and for polishing the final effluent [1].

The mercury from the mentioned sources finds its way to wastewater treatment plants and in some cases increases the mercury level many times above the natural

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background. Since in most municipal wastewater treatment plants biological treatment is applied to stabilize organic and inorganic substances, it is necessary to understand clearly the mercury influence on these processes.

In usually applied techniques to treatment of a mixture of municipal and industrial wastewater, mercury is only partly removed. According to OLIKER et al. [7] the highest efficiency of mercury reduction is achieved by applying activated sludge methods due to adsorption of mercury on the activated sludge.

NELSON et al. [5] have concluded that 5–20% reduction of mercury occurs in the primary sedimentation basin, and the additional 10–80% reduction in the activated sludge process. The authors suggest that the *equilibrium distribution of heavy metals between bacterial solids and solution is mediated primarily by physico-chemical factors and is not influenced greately by active biological processes.* Several authors [2], [5], [6] have shown that the adsorption of heavy metals by activated sludge bacteria occurs rapidly, reaching the equilibrium in 1–2 h after dosing. According to CHENG et al. [2], the uptake of heavy metals at low concentrations results from the formation of metal-organic complexes. At high heavy metal concentrations, however, the metal ions are additionally removed by precipitation.

Investigations on the influence of organisms on the fate of mercury in aquatic environment [3] show that the rate of elemental mercury release into the atmosphere during aerobic incubation is not negligible. During ony day incubation about 1.2% of the added mercury ions have been released at the rate of 160 ng Hg/g sediment/day. Microbial activity according to the authors mediates the reduction of mercury ions to elemental mercury. In principle, the same results concerning the mechanism of mercury uptake are obtained for two types of tolerant bacteria. Reduction of Hg^{2+} to Hg^0 by dehydrogenase has been reported [4]. It is known that the adaptation phenomenon is significant as far as the toxicity effect of heavy metals on biological wastewater treatment processes is concerned [8]. Several authors reported the apparant adaptability of algae to high concentrations of mercury. For example, the algae *Chlorella* growing in mercury chloride concentration of 1000 $\mu g/dm^3$, which does not produce detrimental effects, would grow successfully when transferred to a medium containing 10000 $\mu g/dm^3$, which would be lethal for unacclimatized algae [9]. However, the authors have concluded that as yet there is no sufficient information about the behaviour of aquatic microorganisms in the mercury containing environemnt.

Mercury uptake in aerobic biological processes is mediated mainly by adsorption. Microbial activity in reduction of mercury ions to elemental mercury is not negligible. Nowadays, there is no precise information about toxicity of mercury and possibilities of the adaptation of microorganisms to its presence, especially in trickling filter. Stating the important role of trickling filter systems for intensification of biological aerobic treatment processes, attempt has been made to get more information about the influence of mercury on such systems.

2. MATERIALS AND METHODS

Effect of mercury on biological aerobic filtration process was evaluated by two bench-scale conventional scheme units (fig. 1). The units were located at controlled temperature of 20±2 °C. The total volume of each filter filled with plastic media

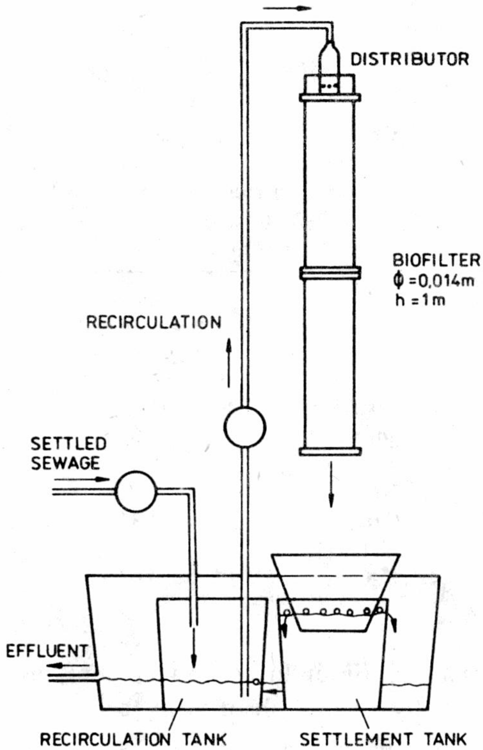


Fig. 1. Schematic diagram of the bench-scale trickling filter system

of the "Flocor" type was 0.0154 m^3. Peristaltic pumps with adjustable speed were used to deliver both the recirculation and feed solutions. The recirculation / feed ratio was 24–25 (feed flow – 17 dm^3/day, recirculation flow – 420 dm^3/day). Feed lines were cleaned daily to prevent microbial growth.

Daily prepared reproducible synthetic wastewater with constant content of organic and inorganic matter was used as feed solution. Its chemical composition is shown in tab. 1. Dextrin and starch were dissolved independently before being added.

Domestic wastewater was used starting up the system.

The achievement of steady-state conditions took about 20 days. Thereupon mercury chloride was added into the feed solution (one filter – at gradually increasing concentrations, and the second one – shock concentrations). The trickling filter system was operated on a daily basis.

TOD, permanganate OD, and pH of the influent and effluent were measured every day, BOD_7 twice a week, and COD once. The analysis included also measurements of the volume of the slime released from the system (performed three times a week) and the weight of the biomass in the filter (performed once a week).

Table 1

Chemical composition of the feed solution used in trickling filter system with recirculation ratio 24–25 (average BOD_7 = 1100 mg O_2/dm^3)

Component	Content g per 20 dm^3 feed solution
dextrin	13.49
glucose	9.00
starch	9.00
NH_4Cl	2.92
$(NH_4)_3PO_4$	1.37
$NaHCO_3$	20.0
K_2CO_3	4.0

The analyses of mercury (in influent and effluent) as well as mercury slime content were carried out by atomic absorption technique. Biomass was observed microscopically every two or three days.

Mercury released from the filter was determined. "Theoretical" detained mercury (T_i) in the biomass was obtained from formula (1):

$$T_i = (V_i(C_{1i} - C_{2i})) - S_i \tag{1}$$

where:

T_i – "theoretical" detained mercury in the biomass during a day i, mg,

V_i – volume of treated solution for a day i, dm^3 (influent volume is equal to effluent volume),

C_{1i} – concentration of the influent during a day i, mg/dm^3,

C_{2i} – concentration of the effluent during a day i, mg/dm^3,

S_i – mercury removed by the process of sloughing, $^0/_0$ (the average value obtained as a ratio of the slime mass removed daily to biomass in the filter).

The released mercury (R) was defined as a difference between the sum of total "theoretically" detained mercury in the system for n days and the mercury content found actually in the biomass in the nth day (formula (1)):

$$R_n = \sum_{i=1}^{n} T_i - F_n \tag{2}$$

where:

$n = 20$, 30 and 49 (the actual concentration of mercury was measured at the 20th, 30th, and 49th days of the treating),

$\sum_{i=1}^{n} T_i$ – sum of total "theoretical" detained mercury in the system for n days, mg,

F_n – actually found mercury in the biomass in the nth day, mg.

3. RESULTS

3.1. REMOVAL AND ACCLIMATION OF ORGANIC SUBSTRATE

The effect of gradually increasing content of mercury in recirculation flow on COD, TOD, BOD, and permanganate OD reduction efficiency can be seen in fig. 2. The results show that the critical concentration for the system is about 1000 μg/dm^3. Up to that point the reduction efficiency remains relatively high. For example, at the mercury concentration not exceeding 950 μg/dm^3 BOD_7, the removal efficiency is above 60%.

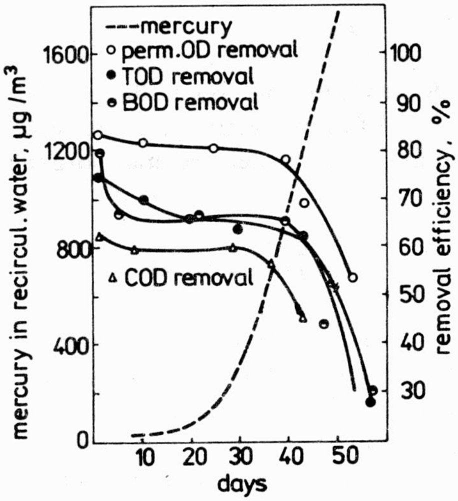
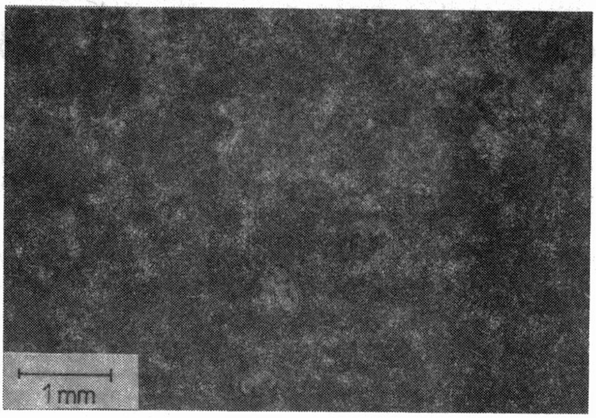
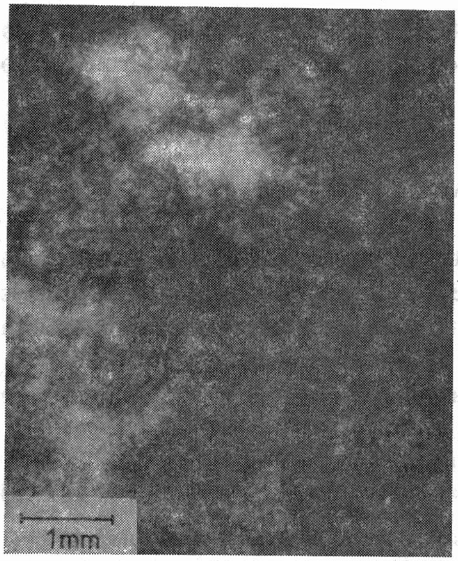


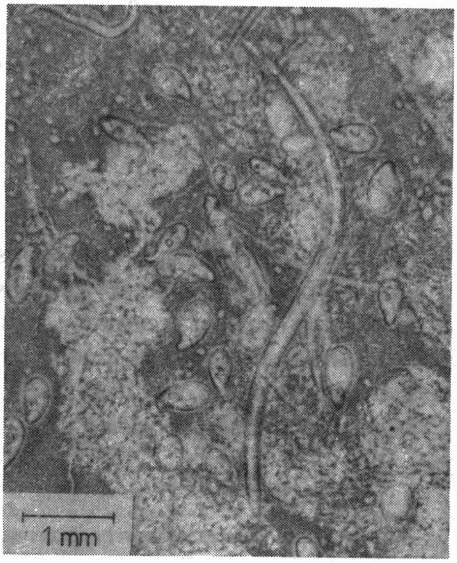
Fig. 2. The effect of gradually increasing mercury concentration on COD, TOD, BOD_7 and permanganate OD removal efficiency



5 – $A_0(B_0)$,

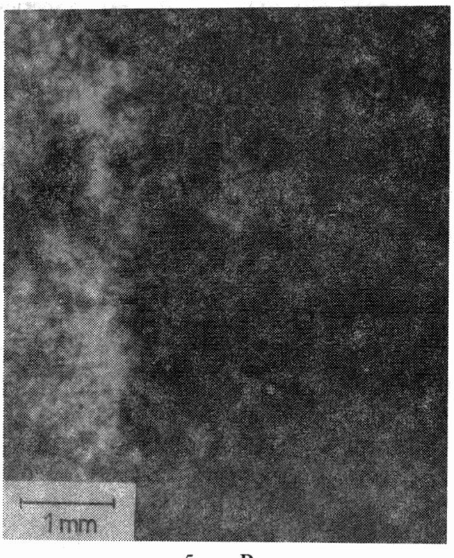


5 – A_1,



5 – A_2,

5 – A_3,



5 – B_1,

Table 2

Comparison of mercury contents in biomass, determined theoretically and found experimentally

Day n	$\sum_{i=1}^{n} T_i$ mg Hg	F_n mg Hg	R_n mg Hg	Mercury released from the system %
20	19.04	17.97	1.07	5.61
30	73.64	70.91	2.73	3.70
49	277.07	260.05	17.02	6.14

amounts calculated theoretically. Most probably this part of mercury was released from the system by microbial activity. Mercury ions were transformed into elemental mercury.

3.3. MICROBIOLOGICAL CHANGES

Biomass in trickling filters consists mostly of bacteria, but it contains also fungi, protozoans and higher organisms. Since it is known that stability of process in aerobic biological treatment is manifested by the predominance of protozoan ciliates, the attention was paid primarily on these microorganisms.

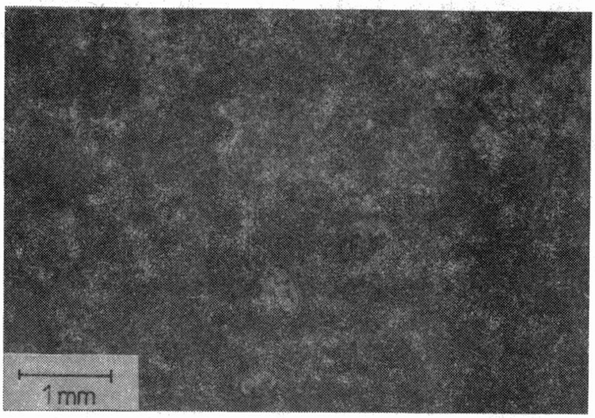
Microscopical observations of the biomass have shown the following main changes of prevailing species (tab. 3).

Table 3

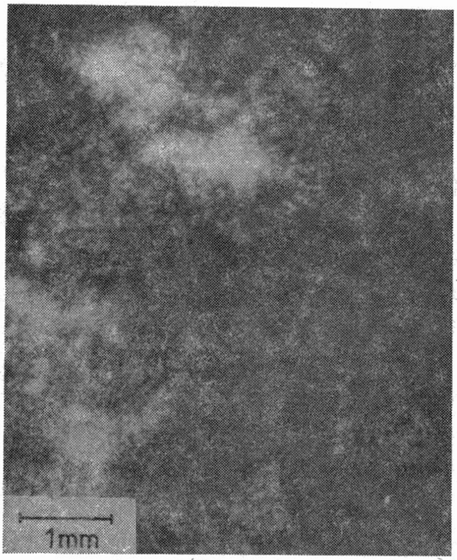
Predominant species of microorganisms in biomass at different concentrations of mercury

Case	Gradually increasing mercury concentration μg/dm³	Predominant species	Case	Shock increasing mercury concentration μg/dm³	Predominant species
A_0	0	ciliates	B_0	0	ciliates
A_1	0–20	ciliates	B_1	0–20	ciliates
A_2	20–90	ciliates + nematodes	B_2	20–90	ciliates + nematodes
A_3	90–900	ciliates + fungi	B_3	above 90	fungi

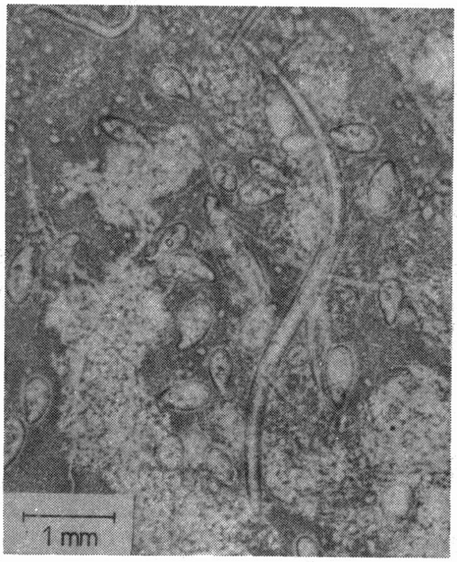
Figure 5 represents typical situations described in tab. 3, i.e. a shift of microorganisms predominant in the biomass during the increasing mercury concentration. It has been observed that at concentrations ranging within 20–



5 – $A_0(B_0)$,

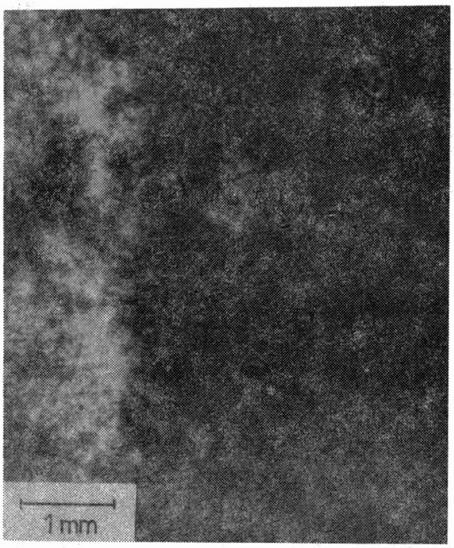


5 – A_1,

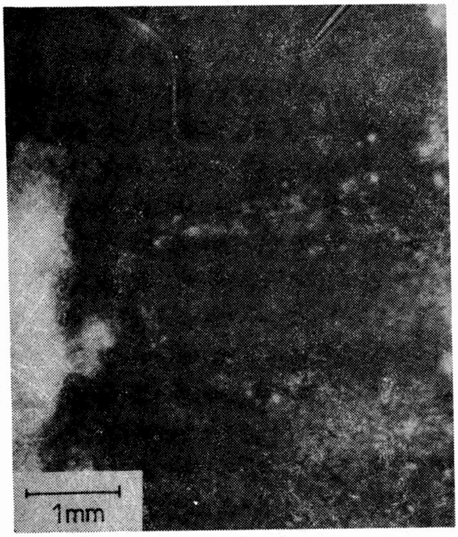


5 – A_2,

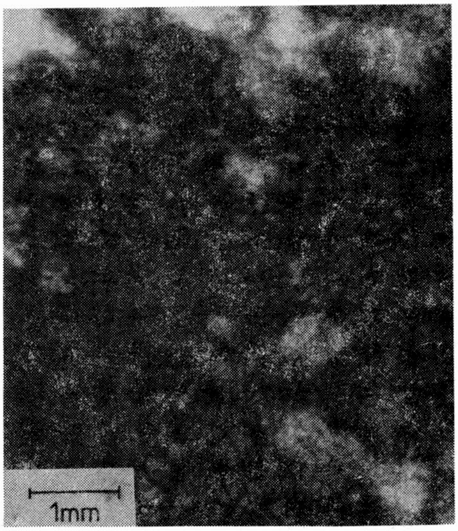
5 – A_3,



5 – B_1,



5 – B_2,



5 – B_3

Fig. 5. Predominant species of microorganisms in biomass at different mercury conctentrations, corresponding to the data presented in tab. 3

90 μg Hg/dm^3, nematodes (higher organisms) become one of the prevailing species. This observation confirmed the effect of adaptation of microorganisms at gradually increasing concentration of mercury.

In the concentrations of 20–90 μg Hg/dm^3 (the case of mercury shock load), ciliates were completely eliminated in contrast to the case of gradually increasing mercury concentration.

4. SUMMARY AND CONCLUSIONS

From the results of the presented experimental study the following conclusions can be formulated:

1. The efficiency of organic matter removal was not significantly affected by mercury concentrations increasing gradually to 1000 μg/dm^3.

2. There exists significant difference in the performance of trickling filter treatment systems at gradually increasing and shock concentrations of mercury.

3. The achieved mercury reduction ranged from 30 to 50%.

4. About 5% of mercury was released by microbial activity.

5. Microscopical observations have shown that mercury when added gradually is due to adaptation not so harmful for protozoans (ciliates) and higher organisms (nematodes) as when shock loads are applied.

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TOKSYCZNOŚĆ RTĘCI W BIOLOGICZNYM OCZYSZCZANIU ŚCIEKÓW NA ZŁOŻACH ZRASZANYCH

Zbadano toksyczność rtęci w biologicznych filtrach aerobowych, stosowanych w laboratoryjnych eksperymentach oczyszczania ścieków modelowych. Ścieki podawane na filtry były powtarzalnymi roztworami wodnymi o stałej zawartości substancji organicznych. Po początkowym okresie wpracowania złoża dodawano do ścieków $HgCl_2$ o stopniowo wzrastającym stężeniu. Osiągnięto 40–60% redukcji substancji organicznych w ściekach, podczas gdy zawartość rtęci nie przekraczała 400 mg/dm^3. Wykonano również testy adaptacji mikroorganizmów do rtęci metodą szoku obciążeniowego. Obserwacje mikroskopowe wykazały zmiany dotyczące głównie pierwotniaków i mikroorganizmów.

ТОКСИЧНОСТЬ РТУТИ В БИОЛОГИЧЕСКОЙ ОЧИСТКЕ СТОЧНЫХ ВОД НА ОРОШАЕМЫХ БИОФИЛЬТРАХ

Исследована токсичность ртути в аэробных биофильтрах, применяемых в лабораторных экспериментах по очистке модельных сточных вод. Сточные воды, подаваемые на фильтры, были повторяемыми водными растворами характеризующимися постоянным содержанием органических веществ. После начального периода врабатывания биофильтра, добавляли к сточным водам $HgCl_2$ с постепенно растущими концентрациями. Достигли 40–60% редукции содержания органических веществ в сточных водах при содержании ртути не превышающем 400 mg/dm^3. Выполнены также тесты приспособления микроорганизмов к ртути методом нагрузочного шока. Наблюдения при помощи микроскопа обнаружили изменения, касающиеся главным образом простейших и высших микроорганизмов.