# Environment Protection Engineering

Vol. 7

1981

No. 2-4

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# THE EFFECT OF ACTIVATED SLUDGE LOADING WITH COPPER ON THE SECONDARY WASTEWATER TREATMENT

The paper presents the results of investigations on the effect of activated sludge loading with  $BOD_5$  and copper on secondary wastewater treatment, in which the most recent methods were employed. The influence of copper on the effluent concentrations of organic carbon, organic hydrogen, and organic nitrogen on the values of dichromate COD, permanganate COD as well as on the composition of activated sludge biomass and its enzymatic activity were determined and the copper cumulation in the biomass was defined. The results may be used in design of industrial secondary treatment plants.

# 1. INTRODUCTION

The rapidly increasing development of the industry creates the necessity of continuous studies in order to establish the methods of wastewater treatment, most efficient from technological and economical view-points. The activated sludge process has been widely applied in treatment of industrial wastewaters.

To establish an optimal course of this process wide technological and biological investigations should be performed. The investigations conducted so far in many scientific centres have usually a technological or ecological character. In the recent years, however, a series of publications have appeared [20], [31], [39], [43], [44] which stated that in order to characterize finally the course of activated sludge the essential factors should be treated as a composite unity.

The investigations undertaken in the present work were to establish the effect of activated sludge loading with copper on the course of biological wastewater treatment and on the activated sludge biomass, employing the most recent methods of analytical control. To this end the experiment was performed in two steps. The influence of activated sludge loading with pollutants expressed in BOD<sub>5</sub> on the efficiency of copper-containing waste-

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water treatment was determined in the first step, whereas the influence of activated sludge loading with copper on the effluent concentration of organic carbon, organic hydrogen, organic nitrogen, dichromate COD, permanganate COD in the treated wastewater, and on the change in the activated sludge biomass, its index, enzymatic activity, and the copper cumulation in the sludge were determined in the second step from several month investigations.

# 2. TOXICITY OF COPPER AND OTHER METALS IN BIOLOGICAL PROCESSES

According to many authors, toxicity is one of the least known but, at the same time, extremely important problem in the domain of wastewater treatment [1], [9], [11], [16], [33], [44], [45]. As an example we may mention the extremely wide range of concentrations of toxic substances assumed by various authors to be admissible. It may be assumed that this is due to different technological parameters of the process, as well as to the differences in criteria used to evaluate the operation of the activated sludge. Very often biological criteria are neglected by the authors who use solely physico-chemical indices, wich eventually leads to erroneous final results. The papers published recently ([8], [9], [18], and [45]) have emphasized that the admissible doses of metals are very difficult to be established and therefore they should be much more carefully admitted than it was before. POON and BHAYANNI [33] have stated that toxic effect of metals changes with the change of biological species. They studied toxic effects of silver, copper, chromium, nickel, and zinc in concentrations of 1-100 mg/dm3 on bacteria and fungus Geotrichum candidum living in water environment. It has been stated that silver and nickel are less toxic for Geotrichum candidum than for wastewater bacteria and that the effects of chromium, copper, and zinc are quite opposite.

JACKSON and BROWN [18] state that despite the investigations performed, there is a great uncertainty as to the long-term effect of toxic compounds, even at low concentrations. The laboratory results obtained by these authors allowed to determine the relationship between the concentrations of a number of metals and organic compounds and their effect on biocenosis.

Investigations carried out by BUCKSTEEG [4] have shown, for instance, that  $CuSO_4$  in concentration of 0.05 mg/dm<sup>3</sup> inhibited the BOD processes and that the concentrations of other metals at which biodegradation processes were inhibited, ranged from 0.1 to 3.8 mg/dm<sup>3</sup>. According to PLACAK, RUCHHOFT and SNAPP [32] copper in concentration of 0.01 mg/dm<sup>3</sup> causes disturbances in biochemical processes. The effect of copper on the course of biochemical process has been also observed by Scott [36] who reports that the value of BOD is not representative at the concentration of copper as low as 0.1 mg/dm<sup>3</sup>.

DIRECTO and MOULTON in [9] emphasize the lack of literature data concerning the influence of variable factors, e.g. loading with organic substances or concentration of

activated sludge in the aeration chamber, on the toxicity of the mentioned metal ions. The investigations performed by these authors were to determine the course of biological treatment at the large initial loadings with copper for different concentrations of activated sludge in aeration chamber.

According to BARTH [3] 5 mg of copper/dm<sup>3</sup> in wastewater affects the operation of activated sludge to the same degree as twice greater loading of aeration chamber with BOD. This author has not, however, examined biological criteria. Negative effect of copper on the activated sludge operation has been chiefly observed in full inhibition of nitrification processes.

According to ZAJACZKOWSKA [45] copper present in wastewater in concentration of 0.8 mg/dm<sup>3</sup> caused disturbances in nitrification processes and decidedly influenced the deterioration of sedimentation conditions of the activated sludge. These observations were confirmed by experiments in which *Paramecium caudatum* was used as the test organism. At the concentration of copper equal to 0.8 mg/dm<sup>3</sup> no living organisms were stated as early as after 5 min. According to SKINNER and WALKER [37] salts of nickel, copper, and chromium at concentrations lower than 1mg/dm<sup>3</sup> inhibit the growth of pure cultures of *Nitrosomonas europacea*.

Many authors emphasize the sensibility of protozoans to toxic compounds ([20], [41], [45]). SUDA and AIBA [41] studied the effect of copper and chromium (IV) on the growth rate of *Vorticella microstoma, Calpidum campylum*, and *Opercularia* sp. They determined ionic concentrations of the mentioned metals at which the growth rate of protozoans was reduced by one half. The concentrations of copper ions amounted to 0.25 mg/dm<sup>3</sup>, 0.32 mg/dm<sup>3</sup>, and 0.27 mg/dm<sup>3</sup> for *Vorticella microstoma, Calpidium campylum*, and *Opercularia* sp., respectively. The corresponding concentrations of chromium, 0.53 mg/dm<sup>3</sup>, 12.9 mg/dm<sup>3</sup>, and 20.29 mg/dm<sup>3</sup>, were higher which results from the toxicity series of metals.

BARTLETT and RABE [2] conducted investigations on the influence of copper, zinc, and cadmium on green algae *Selanastrum capricornutum*. Algicidal concentrations of copper, zinc, and cadmium amounted to 0.30, 0.70 and 0.65 mg/ dm<sup>3</sup>, respectively. Thus, copper exhibited the most toxic effect.

It appears that zinc in concentration of  $0.7 \text{ mg/dm}^3$  acts as an algicide, while in concentration of  $0.1 \text{ mg/dm}^3$  it inhibits the growth of *Selanastrum capricornutum*.

Toxic effect of metals consists also in their cumulative ability. The papers concerning the cumulation of heavy metals by various aquatic organisms are more and more frequently encountered. The mechanisms of such a cumulation are not yet completely recognized. KAGAN and SHTABSKII [19] distinguish three types of cumulation of toxic compounds: material, functional, and mixed one.

According to this systematics, cumulation of heavy metals is classified among the material type. This cumulation is characterized by the fact that the poison leaves the receptor field in a chemically unchanged state and that the receptors regain the state in which they are able to perform their original biochemical and physical functions.

The phenomenon of biocumulation found its practical application in biological ex-

traction of precious metals present in small amounts in ores or waste materials. This is especially important in the case of bacterial acumulation of uranium and silver [35]. The cumulation of metals by activated sludge is also used in removal of metals from wastewaters ([28], [40], [42]).

## 2. EXPERIMENTAL

### 2.1. CONCEPT AND METHODS OF INVESTIGATIONS

Experimental part of the work was devoted to the analysis of the treatment process of copper-containing wastewaters with activated sludge. For various BOD loadings and various sludge loadings with copper, considering the efficiency of copper-containing wastewater treatment, the most advantageous loading of activated sludge was chosen and the effect of copper on the secondary wastewater treatment determined.

The investigations have been performed on a laboratory scale, using synthetically prepared wastewaters, the composition of which corresponded to that of the average municipal wastewaters. At the first stage of the wastewater treatment the process was conducted at the increasing loadings of the activated sludge with BOD and copper. In result of these investigations it has been stated that the optimum loading of the activated sludge with BOD — from the view-point of the process efficiency — amounted to  $0.37 \text{ g/g} \cdot \text{MLSS} \cdot \text{day}$ . At the second stage of copper-containing wastewater treatment the process was conducted at the constant loading of the activated sludge with BOD, equal to  $0.37 \text{ g/g} \cdot \text{MLSS} \cdot \text{day}$ , and at increasing loading with copper. As a result the influence of copper on the course of treatment processes has been also established, the duration of the separate experimental run amounted to about 2 months. Moreover, the range of admissible loading of activated sludge with copper was defined.

- At the first stage the following technological parameters were employed: activated sludge loading  $-0.3-1.0 \text{ g/BOD}_5/\text{g}\cdot\text{MLSS}\cdot\text{day}$ , aeration tank loading with BOD<sub>5</sub>  $-900-3,000 \text{ g}\cdot\text{BOD}_5/\text{m}^3\cdot\text{day}$ , average concentration of MLSS in aeration tank  $-3000 \text{ g/m}^3$ , concentration of copper in the inflow  $-0.4-1.0 \text{ g/m}^3$ .
- At the second stage these parameters were the following: average loading of activated sludge  $-0.37 \text{ g}\cdot\text{BOD}_5/\text{g}\cdot\text{MLSS}\cdot\text{day}$ , aeration tank loading with  $\text{BOD}_5$  – about 1100 g $\cdot\text{BOD}_5/\text{m}^3\cdot\text{day}$ , activated sludge with copper  $-0.53-1.3 \text{ g/g}\cdot\text{MLSS}\cdot\text{day}$ , average concentration of MLSS in aeration tank  $-2900 \text{ g/m}^3$ .

# 2.2 SCOPE AND METHODS OF THE ANALYTICAL CONTROL OF THE PROCESS

#### I STAGE OF INVESTIGATIONS

#### a. Physico-chemical indices

To estimate the course of biological treatment of copper-containing wastewater the following pollution indices have been controlled:  $BOD_5$ , dichromate and permanganate COD, ammonium nitrogen, nitrite nitrogen, nitrate nitrogen, organic nitrogen, pH, temperature, and copper content. The above indices were measured and determined according to HERMANOWICZ et al. [14].

#### b. Technological parameters

The following technological parameters of the process have been determined according to GANCZARCZYK [13] and IMHOFF [17]: concentration of activated sludge in aeration tank, dissolved oxygen content, settling ability of the sludge, sludge index of Mohlman, hydraulic loading, aeration time, activated sludge loading with  $BOD_5$ , and aeration tank loading with  $BOD_5$ .

#### c. Biological investigations

The investigations included macroscopic and microscopic observations of activated sludge.

#### **II STAGE OF INVESTIGATIONS**

#### a. Physico-chemical indices

At this stage to estimate the course of copper-containing wastewater treatment the following indices have been determined: organic carbon, organic hydrogen, dichromate COD, permanganate COD, organic nitrogen, ammonium nitrogen, nitrite nitrogen, nitrate nitrogen, pH, temperature, and dissolved oxygen content.

Organic forms of carbon, hydrogen and nitrogen have been determined by means of elementary analysis on microanalyser Perkin-Elmer, model 240.

The remaining indices have been determined according to HERMANOWICZ at al. [14].

#### b. Technological parameters

The following parameters have been examined: loadings of activated sludge with  $BOD_5$  and copper, loading of aeration tank with pollutants, concentration of activated sludge in aeration tank.

#### c. Biological and biochemical examinations

Biological analysis of activated sludge included macroscopic observations, measurements of the sizes of flocks, and quantitative and qualitative analyses of activated sludge organisms based on microscopic observations performed according to the method developed by Bożko. The following groups of organisms have been observed: *Bacteriophyta*, *Protozoa*, *Fungi*, *Rotatoria*, *Nematodes*, *Oligochaeta*, and *Arachnoides*.

The investigations included also the measurement of dehydrogenaze activity of activated sludge, according to the modified TTC method [22], [34], and determination of copper cumulation in biomass by atomic spectroscopy method [35].

#### 2.3. RESULTS

### 2.3.1. STAGE I

I stage included the experiments aiming to choose the optimum loading of activated sludge with  $BOD_5$  for the treatment of copper-containing wastewaters. The investigations on the efficiency of the copper-containing wastewater treatment with activated sludge have been conducted at sludge loading with  $BOD_5$  ranging from 0.3 to 1.0 g·BOD<sub>5</sub>/g·MLSS·day and at the copper concentration in the inflow varying from 0.4 to 1.0 g/m<sup>3</sup>, which corresponded to the loading of activated sludge with copper from 0.53 to 1.2 mg Cu/g·MLSS·day.

The chosen range of copper concentrations was not an accidental range. The lowest concentration corresponded to that causing no disturbance in the operation of activated sludge, whereas the concentration of 1.0 g/m<sup>3</sup> was already toxic [45]. The experiment included 13 runs differing in concentration of copper in the inflow and in loading of activated sludge with BOD<sub>5</sub>.

The detailed analysis of all the results from these runs allowed to state that at the sludge loading amounting to  $0.37 \text{ g} \cdot \text{BOD}_5/\text{g} \cdot \text{MLSS} \cdot \text{day}$  the treatment effects expressed in BOD<sub>5</sub>, dichromate and permanganate COD removal were the highest, and that for the admissible concentrations of copper in wastewater the course of nitrification processes was regular. Sedimentation of the activated sludge was satisfactory, the sludge volume index was low (within the range of 100 ml/g) and therefore this loading has been recognized to be optimal within the range of conventional loadings.

In view of the above fact it appeared necessary to perform further investigations in order to determine the effect of activated sludge loaded with copper on the course of secondary wastewater treatment for the selected optimal  $BOD_5$  loading of activated sludge.

## 2.3.2. STAGE II

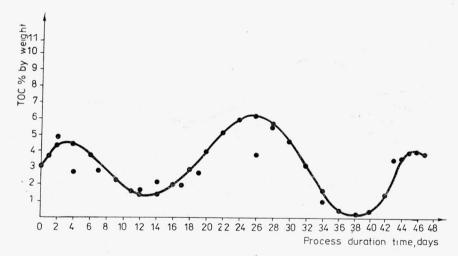
II stage of experiments comprised determination of the effect of activated sludge loading with copper on the process of wastewater treatment with activated sludge.

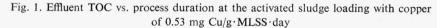
As already mentioned in section 2.1 the effect of activated sludge loading with copper on the course of secondary wastewater treatment has been determined for the optimum loading of activated sludge with BOD<sub>5</sub> equal to 0.37 g/g·MLSS·day, which has been chosen with respect to the efficiency of the process and biological criteria. Moreover, the influence of the activated sludge — copper contact time on the course of the process has been also established.

The investigations at this stage were initially conducted at the activated sludge loading with copper of 0.53 mg Cu/g·MLSS·day. This loading, according to the author's own

investigations and literature data [43-45], should not affect the process of secondary wastewater treatment. Since, most usually the experimental runs last for two weeks, the problem of a long-term effect of copper remains not explained. Therefore, the experiments in this run were performed for about 2 months in order to get more information and to answer the question whether a long-term action of copper on activated sludge is harmful. On the average the removal of the basic pollution indices amounted to 90% for organic carbon, 80% for organic hydrogen, about 80% for dichromate COD, and 84% for permanganate COD.

Nitrification processes proceeded regularly. Decrease of organic nitrogen concentrations amounted to about 60% on the average. Fig. 1 presents the effluent organic carbon concentrations depending on the process duration. As it may be seen, the curve runs irregularly, the dependence varies periodically. Deterioration of results occurring after 3 days may be explained by adaptation of activated sludge to the interaction with copper. Thereupon the results are improved, but at about the 26th day of experiment they deteriorate again and this situation is repeated in 20-25 day intervals. The above described course of carbon reduction is a result of a long-term interaction of copper and activated sludge.



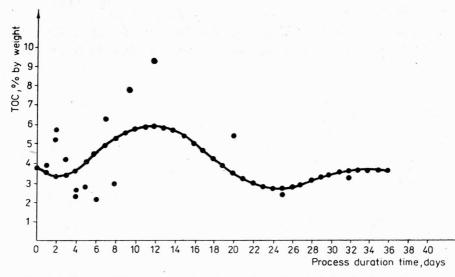


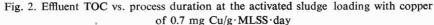
Rys. 1. Zależność zawartości całkowitego węgla organicznego w ściekach oczyszczonych od czasu trwaniaprocesu przy obciążeniu osadu czynnego ładunkiem 0,53 mg Cu/g·s.m. dzień

Apart from the above critical periods lasting for a few days, the results of wastewater treatment for this range of the sludge loading with copper are good. The removal courses for organic nitrogen, permanganate and dichromate COD have a similar character.

The nitrification processes at the given loading of activated sludge with copper ran regularly. During the treatment 1st and 2nd phases of nitrification processes have been observed. Removal of organic nitrogen amounted on the average to about 60%.

After all the results were analysed it has been stated that this loading is not toxic for activated sludge. Therefore, the next series of experiments on a long-term interaction of copper and activated sludge have been carried out at the copper loading equal to 0.7 mg  $Cu/g \cdot MLSS \cdot day$ . The average removal percentage of separate pollution indices is lower as compared to the previous runs. So, for instance, for TOC it equals 77%, for organic hydrogen -73%, for dichromate COD -78.8%, for permanganate COD -80%, and for organic nitrogen -58%. Results of physico-chemical analyses made in this run are presented in fig. 2 which shows the effluent concentration of TOC.. Deterioration of the effluent quality occurs in the time interval ranging from 2 to 12 days of experiment, the second critical period takes place between 28-30 day. In general, the results are worse when compared to the analogical curve presented in fig. 1 for the sludge loading with copper equal to 0.53 mg Cu/g·MLSS·day.





Rys. 2. Zależność zawartości całkowitego węgla organicznego w ściekach oczyszczonych od czasu trwania procesu przy obciążeniu osadu czynnego ładunkiem 0,7 mg Cu/g·s.m. dzień

Nitrification processes in this run are not disturbed. Removal of organic nitrogen is pretty high, the increments of ammonium and nitrate nitrogen are smaller. The results of physico-chemical analyses, despite some premises, do not indicate the toxicity of this copper loading with respect to activated sludge. Hence, it has been decided that in the next run the loading of activated sludge with copper will be increased up to  $0.8 \text{ mg Cu/g} \cdot \text{MLSS} \cdot \text{day}$ . In this run the results of analyses are, in general, not worse than in the preceding ones. They do not correspond to the values which ought to be obtained by treatment of wastewater in activated sludge process within the range of sludge loadings and at the average aeration time anounting to 6 h. This refers in particular to nitrogen compounds.

Fig. 3 represents the dependence of the effluent TOC on the process duration. For the discussed loading of activated sludge with copper the course of the curve is fairly soft, the average percent of TOC removal amounts to about 76% and that of organic hydrogen - to 70%.

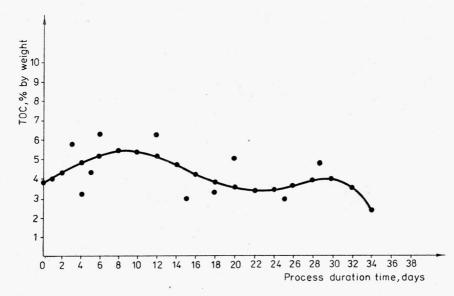


Fig. 3. Effluent TOC vs. process duration at the activated sludge loading with copper of 0.8 mg Cu/g·MLSS·day

Rys. 3. Zależność zawartości całkowitego węgla organicznego w ściekach oczyszczonych od czasu trwania procesu przy obciążeniu osadu czynnego ładunkiem 0,8 mg Cu/g·s.m.·dzień

The values of permanganate COD in the effluent — except for the initial 3-4 days — are more or less alike, ranging within 15.0-16.0 mg  $O_2/dm^3$ , whereas the results of analyses of nitrogen compounds are alarming. The concentration of ammonium nitrogen, considered to be the best source of biogenic nitrogen, was on the average by several miligrams lower than in the former run; nitrite nitrogen occurs in trace amounts. The removal of organic nitrogen in wastewater substantially dropped, being scarcely equal to 44%, whereas in former run it amounted to about 60%. The above results are indicative of disturbances in nitrification processes, being probably due to the overloading of activated sludge with toxic compound, but the answer to this question should be given by the results of biological and biochemical analyses which will be discussed later.

Fig. 4 represents the dependence of the sludge volume index on the process duration at different loadings of activated sludge with copper.

Biological tests included — as given in item 2.2 — macroscopic and microscopic observations of activated sludge and characteristics of its biocenosis participating in the copper-containing wastewater treatment, based on the quantitative composition of the organisms.

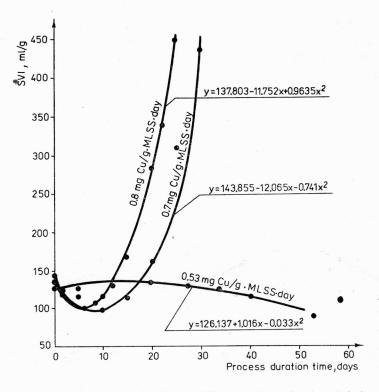
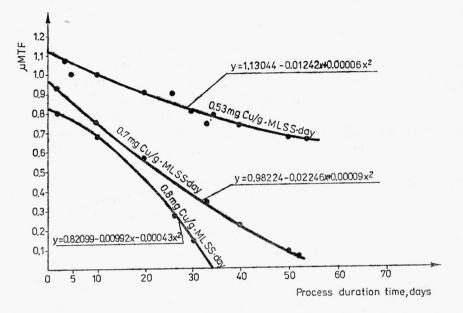


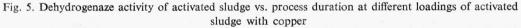
Fig. 4. Sludge volume index vs. process duration at different loadings of activated sludge with copper Rys. 4. Wpływ indeksu osadu czynnego na czas trwania procesu przy różnych obciążeniach osadu czynnego ładunkiem miedzi

The following groups of organisms have been determined: Bacteriophyta, Fungi, Mastigophora, Ciliata, Rotatoria, Nematodes, Oligochaeta, and Arachnoides. Among Bacteriophyta Spirillum, Sphaerotilus, and Zooglea genera have been distinguished. To illustrate fully the influence of activated sludge loading with copper on the course of purification process, the biomass enzymatic activity and copper cumulation in the activated sludge have been measured in all the experimental runs.

Enzymes are a group of proteins particularly important from biological view-point, being the catalysts of a living cell. Many enzymes may get more or less intoxicated due to the influence of some substances. Blockade of respiratory enzyme by cyanides and heavy metals is the known example of such an intoxication ([21], [30]). In the experiments a dehydrogenaze activity of activated sludge was determined.

Fig. 5 represents the dependence of dehydrogenaze activity of the activated sludge on the process duration for various sludge loadings with copper. From the dependence presented it is easily seen that a long-lasting contact with copper, even at a low copper loading, the activity of the biomass at the end of the run dropped by about 30% with respect to the initial one. Much interesting results have been obtained while determining the cumulation of copper in biomass. In the experimental runs at the loading of 0.53 mg  $Cu/g \cdot MLSS \cdot day$ , copper cumulation in biomass amounted to 1.3 mg  $Cu/g \cdot MLSS$  after 28 days and to 2.45 mg  $Cu/g \cdot MLSS$  after 51 days, at the end of experiment.





Rys. 5. Wpływ aktywności dehydrogenazy osadu czynnego na czas trwania procesu przy różnych obciążeniach osadu czynnego ładunkiem miedzi

In the experimental run at the loading of 0.7 mg  $Cu/g \cdot MLSS$  copper cumulation in biomass after 33 days and 51 days was as high as 2.2 mg  $Cu/g \cdot MLSS$  and 3.3 mg  $Cu/g \cdot MLSS$ , respectively.

The results obtained are not numerous due to the much complicated analytical methods and to the application of the unique outfit. High accuracy of results allows, however, to formulate some conclusions. The results obtained from physico-chemical, technological, and biochemical measurements have been analysed by interpolation with the polynomial of N order.

## 3. DISCUSSION

The investigations conducted allowed to determine the changes occurring in the course of secondary wastewater treatment with activated sludge and in the composition of its biocenosis evoked by the presence of copper. The optimal technological parameters have

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been established for the treatment of copper-containing wastewater. This may find a practical application, especially in the copper mine region.

The results obtained in the present work have explained, among others, such essential problems, as the influence of a long-term presence of copper, the effect of activated sludge loading with BOD<sub>5</sub> and copper on the course of treatment process and on the composition and development of activated sludge biomass, and allowed to determine the limiting loadings of activated sludge with copper. The assumed loading of activated sludge with organic pollutants, ranging within 0.3-0.4 g BOD<sub>5</sub> g/g·MLSS day proved to be optimal from the view-point of the process efficiency expressed in the removal of basic pollution indices, as well as considering the biomass composition of the activated sludge. The fact that very high loadings of activated sludge promote the dominance of bacterial forms characterized by disadvantageous sedimentation properties and that flocculent forms readily undergoing sedimentation prevail at the medium loadings was confirmed by the literature data [23].

The results obtained during several month experiments have allowed to formulate some essential conclusions which should be taken into acconut in design of secondary treatment plants for this specific type of wastewater. The intervals of activated sludge loadings with copper have been chosen, basing on all the criteria according to which the operation of activated sludge could be characterized. One of the assumptions made in this paper was to emphasize the importance of such a parameter as the loading of activated sludge with specific compounds. The notion of permissible concentration of toxic compound in activated sludge, encountered in the literature, may only give an information, i.e. what amount of the given compound falls to the wastewater volume unit. The only criterion that gives a complete information in the case of wastewater treatment with activated sludge is its loading with toxic compound, the amount of the latter being given in grams per one gram of dry matter and day.

Summing up, it should be stated that for a complete estimation of the efficiency of wastewater treatment proceeding in time, it is necessary to perform the complex technological and biological tests of the activated sludge. The complete estimation and control of the treatment process — as already stated — should take account of and interconnect all the accompanying phenomena and changes in physico-chemical properties of the wastewater being treated, technological parameters of the process, and composition of the activated sludge. The measurement of the enzymatic activity of biomass by the TTC test is much essential, as its result is closely connected with the population of bacterial flora [34].

## 4. CONCLUSIONS

1. The investigations performed have confirmed the known opinion, namely, that the activated sludge loading with organic pollutants is a decisive technological parameter affecting the efficiency of the treatment process and development of the given biocenosis of the sludge.

2. In results of the experimental secondary treatment of copper-containing wastewater (0.4-1.0 mg Cu/dm<sup>3</sup>) it has been stated that the loading of activated sludge with 0.37 g  $BOD_5/g \cdot MLSS \cdot day$  assures high treatment effects (expressed in  $BOD_5$ , dichromate COD and permanganate COD removal), a correct course of nitrification processes of the first and second phases, and a good sedimentation of the sludge.

3. Loading of activated sludge with metal compounds should, in every case, be preceded by detailed technological tests, because of inhibitory effets of metals on enzymes, in particular, on the respiratory ones. As it follows from the investigations performed, the permissible loading of activated sludge with copper should range within 0.5-0.6 mg Cu/g·MLSS·day. It has been recognized as a limiting loading, since it assures good effects of treatment, appropriate development of biocenosis, and adequately high activity of the activated sludge. In the case of a long-term action of copper, the loading of 0.8 mg Cu/g·MLSS·day should be considered dangerous, because of its disadvantageous effect on the structure and settling properties of activated sludge and its contribution to the reduction of the number of species.

4. It has been stated that the changes in the effluent concentrations of organic carbon, organic hydrogen, permanganate COD, and dichromate COD during copper-containing wastewater treatment process take a regular course. The values of the above indices vary periodically; after 3-4 days of the process the results of treatment are deteriorated due to the acclimatization of activated sludge to the operation conditions (copper); thereupon, the results improve, giving satisfactory effects of treatment, and deteriorate again after 3-4 weaks. The latter is probably due to the fact that the cells damaged by copper are excluded from the process and create a secondary pollution.

5. Long-term toxic effect of copper, even in very small amounts, is more dangerous for the activated sludge than a short-term high loading of the activated sludge with copper, because of its cumulative ability. Therefore, the secondary treatment of copper-containing wastewater should be preceded by technological, biological, and biochemical tests conducted for several months. A two-week period assumed by some scientists for a series of experiments is not reliable when the admissible loadings are to be determined.

6. In the case of copper-containing wastewater treatment with activated sludge, the culture of the latter should be conducted in special tanks operated in parallel to the regular aeration tanks, since due to the microbial ability of copper cumulation the sludge should be exchanged after several months of a continuous operation.

#### REFERENCES

- [1] ARGO D. G., CULP G. L., Heavy metals removal in wastewater treatment processes, Water Sewage Works, Vol. 8 (1972), p. 119.
- [2] BARTLETT L., RABE F. W., Effects of copper, zinc and cadmium on Selanastrum capricornutum, Wat. Research, Vol. 8 (1974).
- [3] BARTH E. F., ENGLISH J., SALOTTON, Field survey of four municipal wastewater treatment plants receiving metallic wastes, J. Wat. Poll. Contr. Fed., Vol. 37 (1965), No. 8.

- [4] BUCKSTEEG W., SCHWEIZ, Ztschr. F. Hydrol., Vol. 22 (1960), p. 107.
- [5] BUTTERFIELD C. T., Studies on sewage purification. II. A zoogloea forming bacterium isolated from activated sludge, U.S. Publ. Hltk. Rep. Wash., Vol. 50 (1935), p. 671.
- [6] CALAWAY W. T., The metazoa of waste treatment processes Rotifers, J. Wat. Poll. Contr. Fed., Vol. 40 (1968), p. 412.
- [7] CURDS C. R., COCKBURN A., Protozoa in biological sewage treatment process. II. Protozoa as indicators in the activated-sludge process, Wat. Research, Vol. 4 (1970), p. 237.
- [8] DERMOTT G. N., MOORE W. A., Effects of copper on aerobic biological sewage treatment, J. Wat. Poll. Contr. Fed., Vol. 35 (1963), No. 2, p. 227.
- [9] DIRECTO L. S., MOULTON E. Q., Some effects of copper on the activated sludge process, Purdue M., 1962.
- [10] ECKENFELDER W. W., GLOYNA E. F., Nowe aspekty projektowania biologicznego oczyszczania ścieków, Gaz, Woda i Technika Sanitarna, Vol. 40, (1966), p. 120.
- [11] ECKENFELDER W. W., MCCABE B. J., Proces design of biological oxidation for industrial waste treatment, Pergamon Press, New York 1959.
- [12] FLETCHER A. W., Metal wiming from low-grade one by bacterial leaching, Trans. Inst. Min. Metal., 1970/79, pp. 247–252.
- [13] GAŃCZARCZYK J., Oczyszczanie ścieków metodą osadu czynnego, Arkady, Warszawa 1969.
- [14] HERMANOWICZ W. et al., Fizyczno-chemiczne badania ścieków miejskich i osadów ściekowych, Arkady, Warszawa 1967.
- [15] HEUKELEKIAN H., LITTMANN L., Carbon and nitrogen transformations in the purification of sewage by the activated sludge process, Sew. Works J., Vol. 11 (1939), p. 752.
- [16] HEUKELEKIAN H., GELLMAN J., Studies of biochemical oxidation by direct methods. Effect of toxic metal ions on oxidation, Sew. Ind. Wast., Vol. 1 (1955), p. 70.
- [17] IMHOFF K., Kanalizacja miast i oczyszczanie ścieków, Warszawa 1970.
- [18] JACKSON S., BROWN M., Effect of toxic wastes on treatment processes and watercourses, J. W. Poll. Contr., Vol. 292 (1970).
- [19] KAGAN Y. S., SHTABSKII B. M., Problem of the molecular mechanisms of cumulation three types of cumulative action of toxic substance, Gig. Sanit., Vol. 11 (1974), pp. 69–73.
- [20] KAŃSKA Z., Badania nad wpływem obciążenia osadu czynnego na kształtowanie się biocenozy w procesie oczyszczania ścieków przemysłowych, Scientific papers, Technical University of Warsaw, No. 22 (1973).
- [21] KARLSON P., Zarys biochemii, PWN, Warszawa 1972.
- [22] KLAPWIJK A., DRENT J., STEENVOORDEN J. H. A. M., A modified procedure for the TTC-dehydrogenase test in activated sludge, Water Research, Vol. 8 (1974).
- [23] LESPERANCE T. W., A generalized approach to activated sludge, part II and III, Water Works and Wastes Eng., Vol. 5 (1965).
- [24] MCKINNEY R. E., Biological flocculation. Biological treatment of sewage and industrial wastes, McCabe, J. Eckenfelder, W. Reinhold, New York 1956.
- [25] LIEBMANN H., Handbuch der Frischwasser und Abwasser Biologie, München 1960.
- [26] MCKINNEY R. E., GRAM A., Protozoa and activated sludge, Sew. Ind. Wast., Vol. 28 (1956), p. 1219.
- [27] MCKINNEY R. E., Microbiology for Sanitary Ingineers, McGraw Hill, New York 1962.
- [28] MING H., PATTERSON I. W., MINEAR R. A., Heavy metals uptake by activated sludge, Wat. Pol. Centr. Fed., Vol. 47 (1975), pp. 362–375.
- [29] PAWLACZYK-SZPILOWA M., Biologia Sanitarna, Wrocław 1970.
- [30] PEISACH J., AISEN P., BLUMBERG W. E., The biochemistry of copper, Academic Press, 1966.
- [31] PIPES W. O., The ecological approach to the study of activated sludge, Advan. Appl. Microbiol., Vol. 81 (1966), No. 77.
- [32] PLACAK O. R., RUCHHOFT C. C., SNAPP R. G., The effect of copper and chromate ions on the BOD of sewage dilutions, U. S. Publ. Health Serv., 1947.
- [33] POON C., BHAYANNI K., Metal toxicity to sewage organisms, J.S.E.D., Vol. 4 (1971), p. 161.

- [34] PRZEWŁOCKI J., Oznaczenie aktywności osadu czynnego, GWiTS, No. 2 (1970).
- [35] SANDELL E. B., Colorimetric determination of traces of metals, Interscience publishers INC, New York 1950.
- [36] SCOTT R. D., Interference with the BOD determination by copper, 4th Ann. Report. Ohio Conf. on Sewage Treatment, 1930.
- [37] SKINNER, WALKER, [in:] Loveles I. T., Painter H. A., The influence of metal ion concentrations and pH value on the growth of a Nitrosomonas strain isolated from activated sludge, J. gen. Microbiol., Vol. 52 (1968).
- [38] SLADECEK V., K ekologiyi infusoriy aktivnogo ila. Otchistka promyshlennych stotchnych vod, pp. 29–37, Moscow 1960.
- [39] SLADKA A., ZAHRADKA V., Morfology of activated sludge, VUV Prace a studie, No. 126, Praha 1970.
- [40] SLOWIK I., Akumulacja miedzi i olowiu przez Sphaerotilus natans i Scenedesmus obliquus oraz zjawiska jej towarzyszące, Institute of Environment Protection Engineering, Technical University of Wrocław, 1976.
- [41] SUDA RYNICHI, AIBA SHUICHI, Effect of copper and hexavalent chromium on the specific growth rate of ciliata isolated from activated sludge, Water Research, Vol. 7 (1973), p. 1307.
- [42] TUOVINEN O. H., Microbiological aspects in the leaching of uranium by Thiobacillus fluorooxidans, Atomic Energy Review, Vol. 10 (1972), pp. 251–259.
- [43] ZAJĄCZKOWSKA-STEMPLOWSKA A., Wpływ wybranych metali na proces oczyszczania ścieków metodą osadu czynnego, Scientific papers, Technical University of Warsaw, 1972.
- [44] ŽAJĄCZKOWSKA-STEMPLOWSKA A., Oczyszczanie ścieków z zawartością soli metali osadem czynnym, Nowa Technika w Inżynierii Sanitarnej, No. 3 (1973), Arkady.
- [45] ZAJĄCZKOWSKA A., doctor's dissertation, Technical University of Warsaw, 1970.

### WPŁYW OBCIĄŻENIA OSADU CZYNNEGO ŁADUNKIEM MIEDZI NA BIOLOGICZNE OCZYSZCZANIE ŚCIEKÓW

W pracy przedstawiono wyniki badań nad wpływem obciążenia osadu czynnego ładunkiem miedzi i BZT<sub>5</sub> na biologiczne oczyszczanie ścieków przy zastosowaniu najnowszych metod. Oznaczono wpływ miedzi na stężenie organicznego węgla, organicznego wodoru i organicznego azotu oraz na wartość utlenialności (dwuchromianowej i nadmanganianowej), jak również na skład biomasy osadu czynnego i jego aktywność enzymatyczną. Określono kumulację miedzi w biomasie. Wyniki można stosować przy projektowaniu biologicznych oczyszczalni ścieków przemysłowych.

#### EINFLUSS DER BELEBTSCHLAMMBELASTUNG MIT KUPFER AUF DIE BIOLOGISCHE ABWASSERREINIGUNG

Der Beitrag beinhaltet die Ergebnisse von Untersuchungen – unter Einbeziehung modernster Analytik – zur Belastung des Belebtschlamms mit Kupfer und  $BSB_5$  und deren Einfluß auf die biologische Abwasserreinigung. Bestimmt wurde der Einfluß des Kupfers auf die Konzentrationen des organischen Kohlenstoffs, des organisch gebundenen Wasserstoffs, des organischen Stickstoffs, sowie des chemischen Sauerstoffbedarfs; desweiter auf die Zusammensetzung der Biomasse sowie deren Enzymaktivität. Bestätigt wurde die Anreicherung des Kupfers in der Biomasse. Die hier dargelegten Erwägungen sollen der Projektierung von industriellen Abwasserreinigsanlagen dienen.

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## ВЛИЯНИЕ НАГРУЖЕНЯИ АКТИВНОГО ИЛА ЗАПАСОМ МЕДИ НА БИОЛОГИЧЕСКУЮ ОЧИСТКУ СТОЧНЫХ ВОД

В работе приведены результаты исследований влияния нагружения активного ила запасом меди и БПК<sub>5</sub> на биологическую очистку сточных вод при применении новейших методов. Определено влияние меди на концентрацию органического угля, органического водорода, а также на значение окисляемости (бихроматной и перманганатной), а также на состав биомассы активного ила и его ферментативную активность. Определена кумуляция меди в биомассе. Результаты можно применять при проектировании станций биологической очистки промышленных сточных вод.