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STUDY OF THE EFFICIENCY OF FERRUM IONS REMOVAL BY AQUATIC HIGHER PLANTS

During aerobic biological treatment of paper mill waste water, the complete treatment of sewage from ferrum ions to the indices of MPC is not provided. Traditional physical-and-chemical treatment technologies are connected with the usage of high-cost, nonrenewable sorbents, which, after treatment, form precipitation which is difficult or impossible to process. Promising alternative is the usage of aquatic higher plants, in particular, Lemna minor (duckweed). In modern research, studying the processes of ferrum ions removal, high level of their elimination is achieved only in 4 – 5 days and is 80±5. The task of reducing the duration of the treatment process is very urgent.

The purpose of this work is to determine the rational parameters of the biological treatment of paper mill wastewater applying the method of active silt (COD, duration of the contact)and study the dynamics of ferrum ions removal in the process of assimilation by Lemna minor (duckweed) (by the duration of the contact and planting density).

Studies were carried out on sewage waters, samples of which were selected at the wastewater treatment plant of the paper mill after the primary sedimentation tanks. Active silt from aeration station was used for aerobic treatment of waste water. Physical simulation was carried out on a pilot plant of SBR reactor type. Ferrum removal was carried out using Lemna minor, in the process of the advanced waste water treatment. Studies of ferrum ions removal dynamics were continued, using test solutions prepared from distilled water with the addition of ferric sulfate.

The obtained results demonstrate regular increase of ferrum ions removal effect at the increase of planting density. The highest efficiency during the first day of the experiment of 88.5% is obtained if the planting density is approximately 5.8g/dm^2, where as the lowest efficiency of 49%, if the planting density is approximately 2.9 g/dm^2. Comparison of the efficiency of sewage and test solutions treatment showed no significant difference, so the presence of pollutants, stipulating the COD index in these conditions does not have a clearly expressed impact on the process of ferrum ions removal. The increase of the planting density significantly influences the intensity of the process, and can be used as the mechanism for reducing the duration of ferrum ions removal from the water.

Keywords: *ferrum ions, lemnoideae, Lemna minor, waste water, treatment, kinetics.*

Problem set up

As a result of the changes of the production technologies, chemical materials used in production processes, range of the manufactured products, alterations of qualitative and quantitive indices of the

industrial sewage is observed, these changes cause the frustration of the processes of sewage treatment and, as a result, lead to their non proper treatment to the level of necessary sanitary norms, acceptable for waste waters disposal into the natural water reservoirs. Serious threat to natural water reservoirs cause biogeneous elements and ions of heavy metals, present in the industrial wastes and residential sewage. In case of aerobic wastewaters treatment of the paper-mill, their proper treatment from iron ions is not provided, their amount remains on the level of 2 mg/dm^3, that exceeds the maximum permissible concentration (MPC), established on the level of 0.3 mg/dm^3.

To solve this problem it is necessary to perform tertiary treatment of sewage effluents. Conventional physical-chemical technologies are connected with the usage of the expensive unrenewable sorbents, which form the precipitation after the treatment, this precipitation is almost impossible to recycle. A promising alternative is the usage of the aquatic higher plants, in particular *Lemna minor* (duckweed), known for its bioremedical properties [1].

Analysis of the latest research

Studies, aimed at the elimination of heavy metal ions by means of aquatic higher plants , in particular, *Lemnaceae* (duckweed family), have been conducted for more than 30 years. Duckweed, *Lemna minor*, possesses high potential for treating surface waters, tertiary treatment of sewage effluents from the wide range of the polluting substances , such as compounds of phosphorus, nitrogen, fluorine, copper, manganese, arcenic, cadmium, nickel, iron, as it is shown in a number of research [2, 3; 4, 5].

It is known that *Lemna minor* grows well and is stable in the environment with the organic pollution and doubles its mass during 5 – 6 days [6].

The studies were conducted on the simulated solutions, surface waters of the lakes, mine waters, waste waters [4, 5].

In the available studies, concerning the elimiation of heavy metals ions, in particular, iron, high degree of its elimination is achieved only in 4 – 5 days and is 80±5%, [4]. The impact of planting density of duckweed on the kinetics of the process and the degree of the ferrum ions elimination was not considered.

The aim of the given study is the search of rational parameters of paper mill waste waters biological treatment by means of aerobic active silt according to COD index and study the kinetics of the process of ferrum ions elimination in the process of tertiary treatment, applying *Lemna minor,* determining on their base, rational duration of the process, duckweed planting density.

Statement of the basic material

Installation, where the studies were carried out, is a clear acrylic container, its internal dimensions are 220X300X47mm, overall dimensions are 220X310X50 mm.

The content of the total iron was determined, by spectrophotometric method, applying ammonium rhodanide by means of spectrophotometer ULAB 102. Weighting of duckweed samples was performed by means of the scale OHAUS Scout Pro SPU 123.

Study of the *Lemna minor* (duckweed) was carried out, using the microscope ULAB X SP-139.

Preliminary studies were performed on the waste waters, samples of which were taken at the water treatment station of the paper mill after the preliminary sedimentation tanks. Indices of the waste water composition were: pH 6.55; NH_4^+ 1.2 mg/dm; NO_2^- 0.038 mg\dm^3; NO_3^- 12.1 mg/dm^3; phosphates 6.5 mg/dm^3; suspended substances 200 mg/dm^3; COD 1300 mg/dm^3; Cl^- 150 mg/dm^3; solid residue 1017 mg/dm^3 [5]. For the anaerobic waste water treatment active silt, taken at Bortnychi aeration plant, was used. Physical modeling was performed at the pilot installation of SBR-type reactor. The complete cycle of treatment aeration – sedimentation – regeneration was one day. The duration of the experiment with the cycle repetitions is 5 days.

The duration of the silt mixture aeration at the dose of the active silt of 2.1 g/dm^3 was studied.

After the aeration COD index of the treated waste water was 520 – 600 mg/dm^3 during 2 – 6 hours of aeration. The greatest effect of the treatment – is 54% if the duration of the process is 3 hours. The period of regeneration was 17 hours (Fig. 1). Within the frame of the given research the concentration of the total iron was determined, it was 1.98 mg/dm^3. After studies of biological treatment (COD 520 mg/dm^3) the investigations dealing with the extraction of the total iron from the water during 1 day with the density of duckweed planting of 20 g/dm^3 were carried out .As a result, the decrease of concentration to 0.93 mg/dm^3 was obtained, treatment effect was 53%.

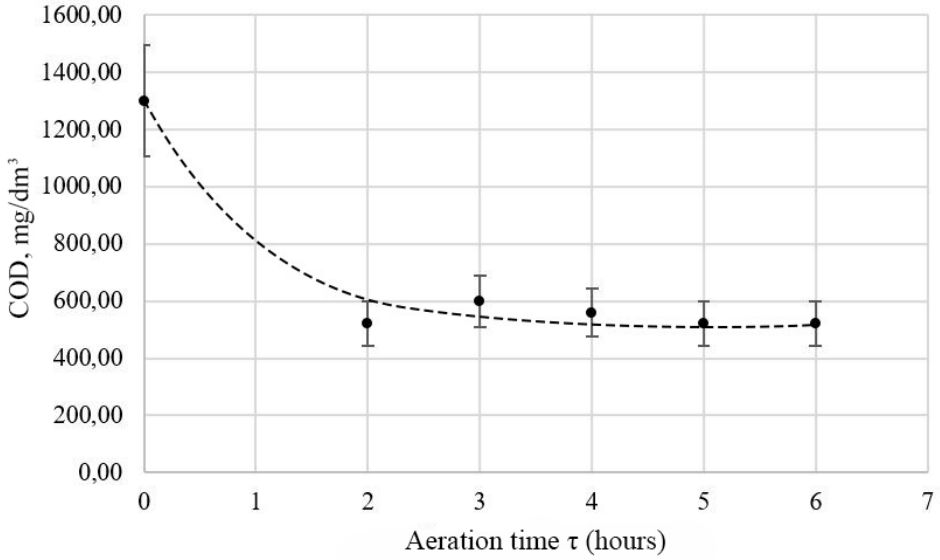
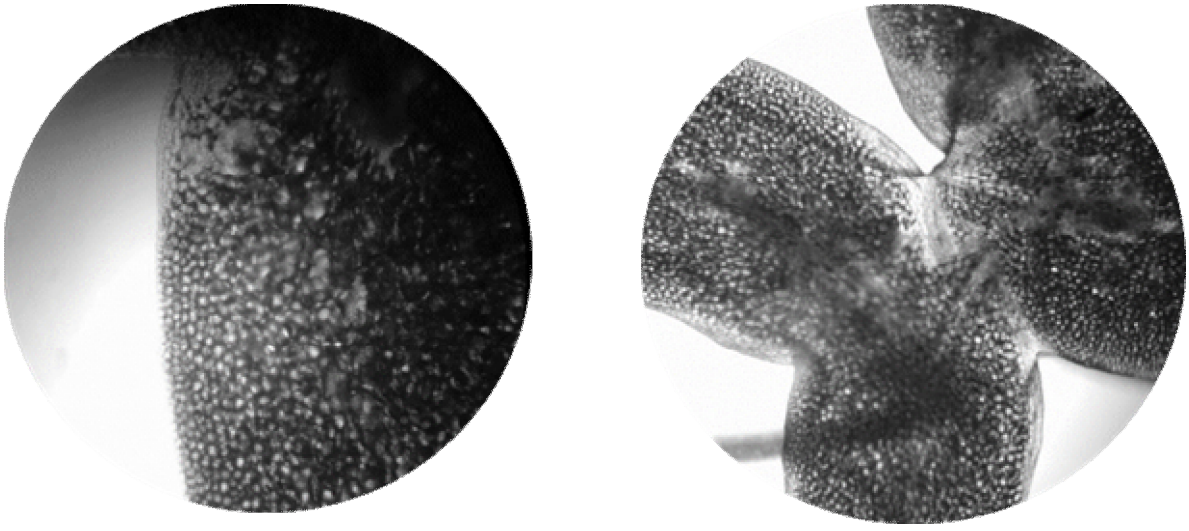


Fig. 1. Kinetics of the waste water treatment process at paper mill according to COD index

Studies of the kinetics of the process were continued, using the simulated solution, prepared from the distilled water with the addition of the ammonium ferric alum ($NH_4Fe(SO_4)_2 \cdot 12H_2O$) in the concentration of 17.28 mg/dm^3 that per ferrum ion is 2 mg/dm^3.

For studies 20, 30 and 40 g of duckweed wet mass (density of planting is 2.9 g/dm^2, 4.4 g/dm^2 and 5.8 g/dm^2, correspondingly) were taken and put into the vessel with 1 dm^3 of the simulated solution. The vessel was under the impact of natural light in the laboratory, air temperature varied within the range of 24 to 28 °C, pH was 7.0±0.2. Samples were taken prior to the beginning of the treatment and at 0.5; 1; 2; 3; 4; 5; 6 and 24 hour of the study and further were analyzed for the presence of ferrum ions. The results are presented in Fig. 3. The error of the method is ±0.05 mg/dm^3.



a) b)

Fig. 2. Vital microscopy of *Lemna minor* prior a) (on the left, magnification 200x) and after the treatment, b) (magnification 100x) of the simulated solutions of the salt $NH_4Fe(SO_4)_2 \cdot 12H_2O$ with initial concentration of 2 mg/dm^3

Lemna minor was taken from the aquarium. By means of the method of the vital microscopy it was studied in order to reveal morphologic changes (Fig. 2.).

Comparing the samples of *Lemna minor* prior to and after the study, partial loss of the green coloring in separate leaves after test solutions was observed. Mechanical damages on the plants were not observed. After carrying out the studies a great number of cells become transparent, thus poor in chlorophyll. Such impact, probably, is caused by the absence of Mg^{2+} ions in the simulated solution, i. e., chlorosis of the fronds occurs.

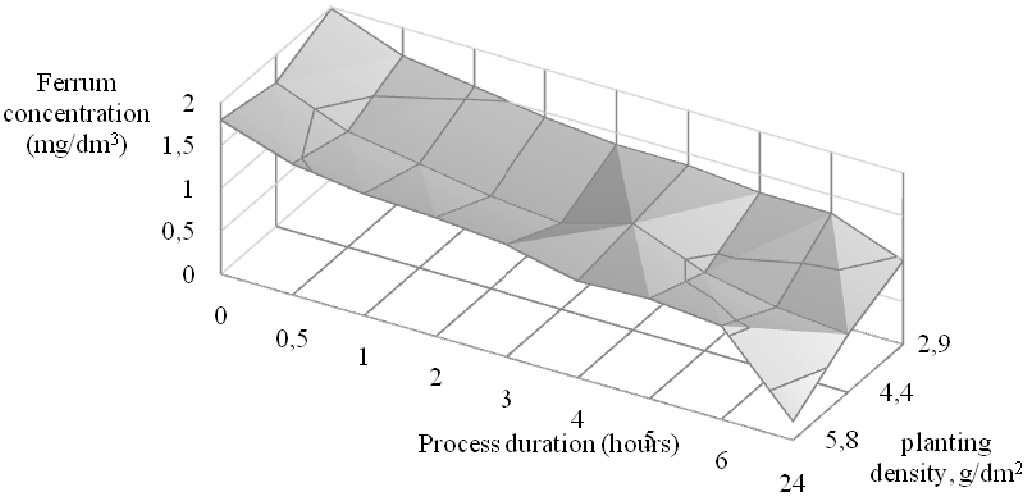


Fig. 3. Dynamics of ferrum ions extraction from the simulated solutions at different densities of Lemna minor planting

According to the results obtained it has been determined that the increase of planting density of *Lemna minor* improves the degree of iron elimination from the water, however if the planting density increases from 2.9 to 5.8 g/dm^2 of the wet *Lemna minor* strict regularity regarding treatment effect increase is observed. It is seen from the results that the kinetics of the treating process at 2.9 and 4.4 g/dm^2 of *Lemna minor* has non-linear character and at 5.8 g/dm^2 of *Lemna minor* has more linear

character, this can be explained by the increase of the apoplast surface, accessible for iron absorption, however, by the simultaneous deceleration of the process of its extraction at the expense of the decrease of the concentration in the solution. Active protein transport is unlikely possible, because the iron is in the form of Fe^{3+}, whereas protein transport is characteristic for bivalent metals.

Conclusions

The obtained results demonstrate normal increase of the treatment degree for the ferrum ions at the increase of the *Lemna minor* planting density. It was revealed that the best effect of the ferrum ions elimination is 88.5% during 24 hours of the treatment at 5.8 g/dm^2 of the wet *Lemna minor,* however, it has, probably, linear character. At its less quantity the decrease of iron compounds extraction effect occurs. In the process of comparison of waste waters treatment and simulated solution considerable difference in treatment effect is not observed , thus the presence of the pollution by COD index in the given waste water does not have considerable impact on the process of ferrum ions extraction. Increase of *Lemna minor* planting density greatly influences the rate of the process and can be applied for the decrease of waste water treatment duration.

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Editorial office received the paper 06.04.2018.
The paper was reviewed 18.04.2018.

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