ECOLOGY

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BIOSORPTION-BIOCOAGULATION DETOXIFICATION OF WASTE WATER BY ACTIVE SLUDGE

In the article it was described a problem of waste water purification from heavy metals. It was proposed biosorption-biocoagulation way of water detoxification at primary settlers by part of active sludge with the aim to decrease heavy metals influence at water treatment. It was shown that the main part of heavy metals of waste water is in colloid-bound form. At studying sorption properties of periphyton and active sludge at different stages of water treatment it was found that active sludge of 1st, 4th corridors of aerotank and sludge camera had a maximum bounding capacity to Fe ions. Biological testing of *E. gracilis* cell's movement made it clear that toxicity level of waste water in primary settlers decreased 5–6 times after biosorption-biocoagulation detoxification, and purified water satisfied nominative demands on toxicity.

Key words: waste water, heavy metals, dispersion analyses, detoxification, sedimentation, active sludge, biosorption, biocoagulation, biotesting.

Introduction. Detoxification of waste water contaminated with heavy metals (HM) is one of the urgent problems of water treatment and improvement of the environment [1–4].

Typical municipal treatment facilities do not provide for a special waste water treatment from heavy metals [1].

Our analysis of the process of detoxification of waste water in different stages of its treatment at Minsk purification plants (MPP) showed that after the sewage tank passage, the toxicity of MPP-1 and MPP-2 waste water is reduced by 15–20% [3].

The activated sludge aeration tank plays the most important role in detoxification of waste water. High content of HM reduces the efficiency of water purification and makes it impossible of using activated sludge as a fertilizer.

In a typical scheme of water treatment there is a sludge chamber between final settling tank and aerotank, where sludge is settled. Sludge chamber is purged with air in order to avoid of sludge precipitation or its appearance on the surface due to denitrification phenomena.

Part of the active sludge from the sludge chamber is assigned to the 1st, 2nd corridors of aeration tank for regeneration and reuse, and the excess is sent to the shop for sludge dewatering and removal.

In this paper we propose to use part of the surplus active sludge for biosorption-biocoagulation waste water treatment from heavy metals.

Main part. The goal of the work is to test the possibility of using active sludge for extra detoxification of sewage in the primary settling tank.

The objects of study were periphyton (PF) [4] and active sludge (AS) selected from the four corridors of the aeration tank and sludge chamber MPP-1, as well as waste water with a concentration of suspended particles of 0.3–0.5 g/l.

For experiments it was used the following equipment: spectrophotometer SPEKOL-1300 centrifuge Hettich Model EVA-2, microscope LOMO EU P11, analytical scales Sartorius CPA225D, membrane installation "Key M" and membrane filters Nerox, CJSC SPA "Simpeks" digital camera Canon Power Shot A3300 IS, as well as software Adobe Photoshop CS3.

To conduct research ferrous sulfate solution, EDTA at concentrations of 10^{-1}–10^{-5} M were used.

Iron was chosen as the object of analysis of distribution of TM, since it is one of the most widespread and common elements in the waste water.

Determination technique of total iron content in accordance with GOST 4011–72 is based on its reaction with sulfosalicylic acid in an alkaline medium to form a complex compound of yellow color, detected at a wavelength of 400 nm (ε = = 14,600 l/mol · cm).

The particulate composition of particles of primary settler waste water was studied by sedimentation, light microscopy, light scattering [5, 6] and proposed method [7].

To determine the particle size and content by the method of sedimentation analysis, waste water samples were placed into the 100 cm^3 cylinders and were recorded the kinetics of sedimentation substances by digital processing of images [7], as well as periodically selecting of 10 cm^3 of water in 10, 30, 60, 90, 120 min and determining the concentration of the particles deposited by weighing the dry residue.

Knowing the rate of deposition and radius of standard particles, the radius of analyzed particles is calculated according to the formula

$$r = r_o \cdot \sqrt{u / u_0}, \quad (1)$$

where u, u_o, r, r_o are deposition rate and the particle size of the standard and analyzed samples.

Precipitated and non-precipitated fractions of waste water particles were obtained by infiltrating water through a membrane filter with a pore diameter of 0.45 μm.

The filtrate was further centrifuged at 1,000–10,000 rpm for 10 minutes in a closable plastic centrifuge tubes $V = 10$ cm^3.

The content and particle size in the supernatant were analyzed by spectrum turbidimetry.

Scattering of light by particles with sizes much smaller than the wavelength of the incident light is described by the Rayleigh equation; and for particles comparable with the wavelength of light, their sizes are determined using Geller equation [5]:

$$D = K / \lambda^x, \quad (2)$$

where D is optical density of the suspension; K is constant; λ is the wavelength of the incident light; x is index associated with the particle size and varying from 4 (for the Rayleigh particles) to 0 (full reflection of light from coarse particles).

The obtained fractions were analyzed for Fe content (Fe_{com}), expressing it as a percentage of the total concentration of different forms in the water.

To characterize the sorption properties of the AS and PF they were preliminarily processed by EDTA (10^{-1} M) for 1–3 hours, washing with distilled water to remove the chelate and extracted TM and used for studying of the binding of the iron ions.

Analysis of the properties of the sorbent was performed in accordance with the monomolecular isotherm sorption of Langmuir equation [6]:

$$A = \frac{A_\infty \cdot K \cdot C}{1 + K \cdot C}, \quad (3)$$

where $A = \Delta C \cdot V / m$ is specific binding capacity; ΔC is concentration difference mol/l; V is volume of the solution of an iron salt, l; m is sorbent mass, g.

After conversion (3) in the inverse coordinates the maximum specific capacity (A_∞) and binding constant (K) were determined.

The influence of active sludge on sedimentation of particles in waste water of primary settler can be judged using the method of analysis of the brightness of digital images [7].

To assess waste water detoxification, the cells of microalgae *E. gracilis* from the collection of the department of biotechnology and bioecology of BSTU were used as test cultures.

The level of toxicity of the medium was assessed by biotesting method of cell mobility, as described previously [3].

Heavy metals may be in the waste water in various forms in the composition of non-precipitating fractions as free ions bound with molecules, colloidal particles, cells of microorganisms as well as in the composition of the deposited fine, medium and coarse fractions.

Choice of purification of waste water from heavy metals depends on their distribution between the fractions of particles. Therefore, the first phase of the work included disperse analysis of waste water particles and study the distribution of iron ions between the factions of the particles of the 1st settler MPP-1.

The data obtained are shown in Table 1.

Table 1 shows that the iron in the waste water of the 1st sedimentation tank is generally in the molecular colloidal form and makes complexes with organic and inorganic materials, whereas the content of free ions in the waste water is considerably smaller than in the bound form. Colloidal particles with a size of 1–100 nm as well as solutions of substances have kinetic stability and do not precipitate into the waste water, while colloidal suspension fraction may be precipitated by prolonged sedimentation.

Suspended particles of size greater than 10 μm are sedimented well during 2 hours of sedimentation in a primary settler.

The most common and easy ways to remove non-precipitable particles are adsorption and coagulation.

As a sorbents and coagulants can be used microorganisms of excess AS and PF, which are the wastes of waste water treatment.

Table 1

Distribution of Fe_{com} between the fractions of the waste water particles of primary settling tank at MPP-1

Fraction	Content Fe_{com}, %	Size of particles	Method for determination of the particle size and content
Non-precipitated and partially precipitated forms			
Ion-molecular	14.7	0.08–10 nm	Spectrophotometer
Molecular colloid	59.0	10–100 nm	Centrifugation, light scattering, microfiltration
Colloidal-suspension	9.1	100–450 nm	
Precipitated forms			
Fine-dispersed	6.6	0.5–10 μm	Sedimentation, microfiltration, light microscopy, scaling
Middle-dispersed	6.0	10–50 μm	
Coarse-dispersed	4.7	50 μm and more	

To evaluate the sorption properties of AS and PF, model solutions Fe^{2+} were added to purified biosorbents and determined A_∞ of their binding. The results are shown in Fig. 1.

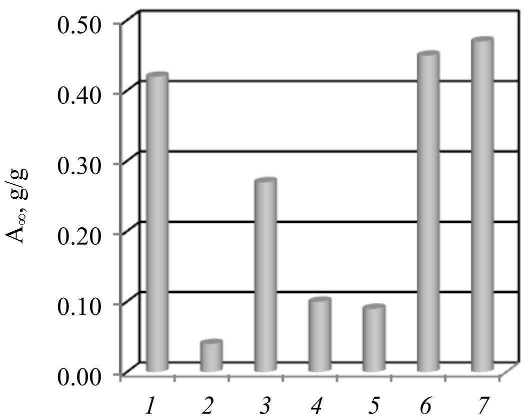

Fig. 1. Characteristics of the specific binding capacity of iron ions by organic sorbents:
1 – AS_1 (1st corridor); *2* – PF_1 (1st corridor);
3 – AS_2 (2nd corridor); *4* – AS_3 (3d corridor);
5 – PF_4 (4th corridor); *6* – AS_4 (4th corridor);
7 – AS_5 (sludge chamber)

As it can be seen from Fig. 1, AS_1, AS_4 AS_5 of sludge aeration tank and the camera have the meanings A∞ of binding iron, significantly higher than for PF.

In the process of biological treatment of waste water in aeration tank it was found that A_∞ parameter for Fe^{2+} binding by microorganisms of AS_2, AS_3 are reduced by 2–5 times compared with AS_1, AS_4. That may be due to sorption on the surface of cell molecules and decrease in the number of available centers for binding of iron ions, as well as changes in the state of AS association in the corridors of the aeration tank.

Four corridor aeration tanks are used on MPP, operating on the principle of the aeration tank of the propellant, with 25–50% regeneration of active sludge. At 25% AS regeneration the 1st corridor of aeration tank is served as a regenerator, where the circulating (return) activated sludge is given.

All waste water purification can be divided into phases, which reflect the processes occurring in the four corridors of the aeration tank.

In the 1st corridor the amount of pollution is small and there is extra oxidation of the adsorbed on AS hard degradable substances. At the same time processes of destruction of the old cells and the formation of new cells occur, the restoration of oxidation, sorption properties of the AS, which is here in the form of flakes.

In the 2nd corridor of aeration tank with mechanically purified waste water, rich in organic matter, the adsorption of substances as the first and the fastest stage of biological treatment is performed. Then low purification stages follow: release of enzymes, digestion and transport of monomers into cells with subsequent catabolism, anabolism and cell proliferation.

In the 3rd passage AS flakes disintegrate with increasing number of single cells, wherein the ratio of surface area/volume increases, which is necessary for increasing transport of organic compounds and stimulation of cell proliferation.

In the 4th corridor of aeration tank and two settling tanks and sludge chamber, the concentration of available organic matter is minimal, the cells are forced to unite in associates to form flakes of AS.

Since the maximum specific binding capacity of HM by microorganisms of AS in sludge chamber is significantly higher than PF, AS_2, AS_3, to remove heavy metals it is advisable to use an excess of the AS, directing it from the sludge chamber into the primary settler.

Since the addition of an excess of the AS can affect the sedimentation of particles in the primary settler, it was necessary to find out the optimal dose of AS, not interrupting this process.

To do this, we inserted different amount of AS into waste water (WW) of the primary settler and the kinetics of particle sedimentation was recorded by digital image processing. Fig. 2 shows the results obtained.

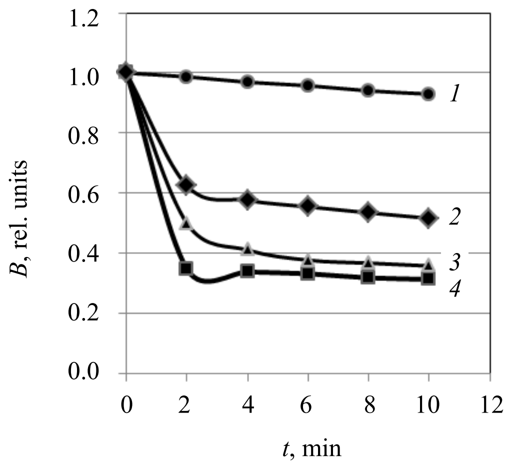

Fig. 2. Kinetics of changes in brightness of digital images in the waste water of the primary settler:
1 – WW without AS; *2* – AS : WW = 1 : 3;
3 – AS : WW = 1 : 6; *4* – AS : WW = 1 : 4

As one can see from Fig. 2, the introduction of active sludge into waste water of a primary settling tank in the ratio 1 : 6–1 : 4 accelerates the sedimentation of the particles, which may be explained by biosorption and biocoagulation properties of AS.

Increasing the dose of AS to 1 : 3 results in deterioration of particle deposition in settling (Fig. 3).

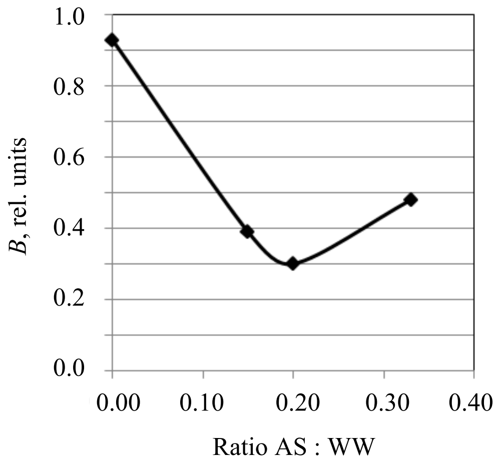

Fig. 3. Changing of the brightness (B) of the digital images of the waste water primary settling tank from ratio of AS : WW

Analysis of changes in the level of waste water toxicity before and after the treatment by excessive AS was made according to the method of biotesting cell mobility with *E. gracilis* (Table 2).

The data from Table 2 showed that biosorption–biocoagulation properties of AS reduces the toxicity index of waste water in 5–6 times.

Increasing doses of AS is added to the primary settling tank, above the ratio AS : WW = 1 : 3 is impractical because in spite of the increase in the detoxification of waste water conditions of sedimentation of suspended particles in the primary settling tank deteriorate (Fig. 3).

Table 2

Biotesting of waste water toxicity in the primary settling tank with cells *E. gracilis*

Samples	Toxicity level, %
Control	45.3 ± 3.0
AS : WW = 1 : 6	20.1 ± 2.3
AS : WW = 1 : 4	10.3 ± 1.9
AS : WW = 1 : 3	8.5 ± 1.2

Toxicity level of waste water reaches a safe level, the relevant point of discharge water into the river Svisloch, which characterizes it as non-hazardous and satisfying the demands of toxicity and safety [3].

Reducing of waste water toxicity level entering the aeration tank will reduce the load on the AS, enhance its activity and improve the quality of water purification.

Conclusion. In the paper was studied the distribution of iron ions on the particle fractions of waste water primary settler at MMP-1.

It was established that most of the iron ions are in the molecular colloidal form, for removing of which it is not enough the normal sedimentation of particles.

It was proposed biosorption-biocoagulation way to detoxify the waste water in the primary settler tanks, using excess activated sludge. That allows 5–6 times to decrease the level of waste water toxicity and reduce detoxifying loading on micro-organisms of the activated sludge in aeration tank; to increase the effectiveness of treatment and reduce the pollution of activated sludge by heavy metals to the level allows to use it as an organic-mineral fertilizer.

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