Macrokinetic Model of Biochemical Oxidation

Vladislava Nikolaevna Volkova and Viktor Leontievich Golovin

Abstract In the Russian Federation, the current standards oblige to carry out not only complete biological treatment of wastewater, but also their additional treatment. The main task of post-treatment technological processes is the removal of biogenic elements and some specific pollutants from water that has undergone biochemical treatment. Thus, the improvement of post-treatment remains an urgent environmental task, and the requirements for it can be defined as follows: ensuring the most complete removal of biogenic and other specific pollutants, including those contained in post-treatment wastewater in the form of colloids; ensuring the safety of discharges into water bodies by reducing the formation of carcinogens during disinfection; ensuring a high cleaning effect with increased instability of waste management conditions; ensuring technological simplicity and reliability of post-treatment devices; ensuring a reduction in the consumption of clean water for restoration work. This paper investigates a method for post-treatment of wastewater by a slow filmless filter with a vertical filtering surface. The properties of the slow filter cassette with respect to ammonium and phosphorus ions have been studied. The analysis of the integral kinetic curves is carried out. The efficiency of additional purification of wastewater from biogenic elements by a filmless slow filter for ammonium and phosphates has been investigated.

Keywords Deep cleaning · Biochemical destruction · Slow filter · Biogenic elements · Substrate inhibition · Stationary processes

1 Introduction

Progress is visible all over the world is noticeable in the field of environmental protection, the most important result of which is the reduction of the negative impact on its condition, in particular, when wastewater is discharged into water bodies. The results of a survey of treatment facilities show that after cleaning, the permissible limits of

V. N. Volkova (✉) · V. L. Golovin
Federal State Autonomous Educational Institution of Higher Professional Education "Far Eastern Federal University" (FEFU), Polytechnic Institute, Vladivostok, Russian Federation
e-mail: vladavibi@bk.ru

P. Akimov and N. Vatin (eds.), *Proceedings of FORM 2021*, Lecture Notes in Civil Engineering 170, https://doi.org/10.1007/978-3-030-79983-0_44

effluent quality indicators, standardized for fishery reservoirs, can be significantly exceeded (5–10 times) [1]. This is due not only to the excess of the permissible load on water bodies, when, with unstable hydrological parameters, the intensity of dilution of treated effluents changes significantly and, therefore, it is not possible to achieve the required degree of their dilution. Often, a more important factor determining the excess of the permissible load is the inconsistency of the cleaning technologies used in practice with modern environmental requirements for the prevention of environmental pollution. During traditional disinfection of insufficiently treated wastewater with chlorine or ozone, chlorine or ozone organic substances, which are carcinogens, enter the water body. Such toxins cause almost more harm to the biocenosis of natural water bodies and watercourses than the discharge of untreated wastewater at all, and the content of residual chlorine, which is incorporated into the structure of organic compounds and loses its active oxidizing properties, does not guarantee absolute epidemiological safety.

2 Methods

In the Russian Federation, the standardization of the load on water bodies is used, with the provision of control of the dispersion or dilution of pollution, which is determined, in particular, by the value of the biological oxygen demand (BODtot) of the treated wastewater. At the same time, this indicator can be assessed as depending on a number of treatment conditions, for example, such as temperature, the content of toxic substances in the treated water, the ripening and aging time of activated sludge, changes in the species composition of microorganisms, as well as the effectiveness of the applied post-treatment methods—tertiary treatment. The main task of the technological processes used in post-treatment is to remove biogenic elements and some specific pollutants from the water that has undergone biochemical treatment. In particular, the role of destruction of microorganisms in the formation of colloidal systems when changing the conditions of their vital activity from aerobic in aeration tanks to anaerobic in secondary sedimentation tanks is not entirely clear. However, like other organic matter, from which only coarse particles are removed in secondary sedimentation tanks without destructive effects. Thus, the main burden of removing the residual amount of nutrients, after biological treatment, which are mainly in the form of a colloidal solution, falls on tertiary treatment.

The technologies used in the world for such purification are very diverse and usually very complex. In countries such as the USA, Australia, and Spain, membrane methods of wastewater treatment are actively used [2, 3]. Such technologies are designed to ensure a more complete removal of pollutants, including biogenic substances. This allows the treated wastewater to be reused, in particular, by discharging it into the reservoirs of the drinking water supply systems. According to the results of a survey of wastewater treatment systems in the United States [4], it can be noted that filtering devices are used quite often in tertiary treatment. However, the greatest effect of removing nutrients is achieved on devices with a floating filter bed

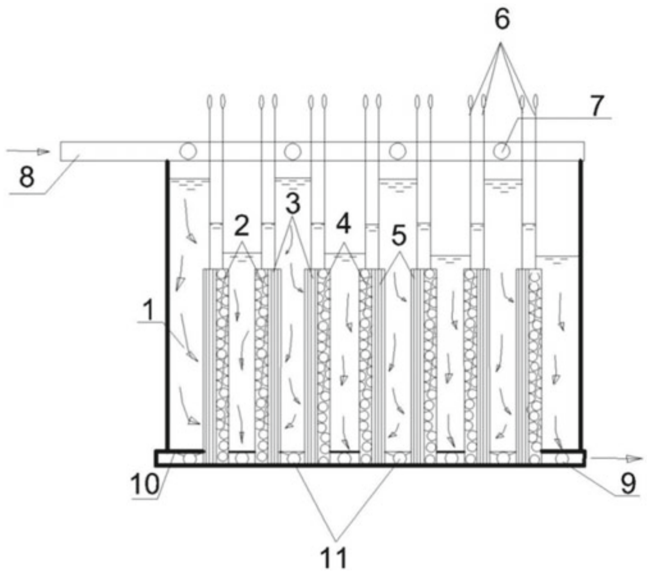
(Placerville) and in adsorbers ("Tahoe Truck" complex). The Taho Trucki complex previously used a slow filter made in the form of a soil tank with a sandy load with a horizontal filtering surface. Despite the high effect of removing impurities of different dispersion during film filtration, this structure had to be abandoned due to technological difficulties during the regeneration of the filter layer. Considering that the main reason for the difficulties of regeneration in such filters is the need to remove silty biofilm from a horizontal surface and, therefore, it was necessary to empty them, dry and replace the top layer of the load, an attempt was made to use removable filter elements with a vertically located filtering surface (radial blocks and flat cassettes) [4]. This design of slow filters allowed to eliminate important technological problems of regeneration of the filter material and to reduce the amount of clean water used.

Despite the high effect of removing impurities of different dispersion during film filtration, this structure had to be abandoned due to technological difficulties in regenerating the filter layer. Considering that the main reason for the difficulties of regeneration in such filters is the need to remove silty biofilm from a horizontal surface and, therefore, it was necessary to empty them, dry and replace the top layer of the load, an attempt was made to use replaceable filter elements with a vertically arranged filtering surface (radial blocks and flat cassettes) [4]. This design of slow filters eliminated important technological problems of filter media regeneration and reduced the amount of clean water used.

In the Russian Federation, in the course of tertiary wastewater treatment, the desire to simplify the process of deep wastewater treatment has determined the widespread use of filtering devices, in particular, rapid filters with granular loading and frame-filling filters [1]. In a filmless slow filter with a filter material thickness of 0.2–0.3 m, biofilm does not form on the frontal surface, and the biomass is relatively evenly distributed throughout the pore volume. Due to this effect, the period of biomass accumulation and, consequently, the duration of the filtration cycle can be increased to one year or more, depending on the content of the residual amount of suspended and colloidal particles after the secondary sedimentation tanks. Thus, in comparison with slow filters with a horizontally located filtering surface, the regeneration period increases by 10–14 times. In this case, when the maximum saturation of the pore space with pollutants is reached, the cassettes are replaced with reserve ones, and the filtering capacity of the material is restored outside the device by drying the accumulated biomass and blowing the cassette with a fan without using purified water. Filmless slow filters with a high degree of additional treatment of effluents and more complete removal of organic matter ensure the ecological safety of water bodies during discharges even after disinfection by chlorination or ozonation. The circuit of a filmless slow filter is shown in Fig. 1.

In order to reveal the effectiveness of a filmless slow filter with a vertical filtering surface, it is necessary to conduct an experiment.

The aim of the experiment was to study the filtering properties of a slow filmless filter cassette with a vertical filtering surface in relation to ammonium and phosphorus ions. To achieve this goal, it is necessary to the following tasks:



1 - case;
2 - branch pipes of the purified liquid supply; 2,3 - cassettes; 4.5 - filter material;
5 - waterproof partitions;
7 - supply pipes; 8 - supply manifold; 9 - outlet turbine;
10 - branch pipes; 11 - drain collector of purified water

Fig. 1 Schematic of a filmless slow filter with a vertical filter surface

- examine the composition of wastewater for the presence of ammonium and phosphates, before and after filtration;
- to build a kinetic model based on research data, to analyze the integral kinetic curves of destruction.

3 Results

Technological parameters of biochemical destruction of ammonium and phosphorus ions in waste water after secondary sedimentation tanks were worked out on a slow filter cassette with a vertical filtering surface of 0.05 m^3 volume. The unit includes a system for supplying and discharging waste water; the cassette consists of two paired cassettes with a filtering load. The first cassette contains a polypropylene fiber filter with a mesh size of 3–5 mm. The second cassette consists of expanded polystyrene granules with a grain size of 2–3 mm. The concentration of ammonium and phosphorus ions is determined according to the methods recommended in the specialized literature: ammonium—with Nessler's reagent, phosphates—with a mixed reagent. Experiments on biological purification of the aquatic environment from ammonium and phosphates were carried out with free-floating microflora. Stationary processes of biochemical destruction were simulated without additional supply of pollutants during the experiment. The primary results of the experiment were points in concentration–time coordinates. All points were averaged over three or four values. The experimental data are given in Table 1.

The shape of the curve allows various statistical descriptions. The dependence presented below is quite complex for analytical presentation. For data analysis, the rate of oxidation is taken, which is defined as the amount of harmful substances removed per unit of time, for any pair of values of concentration and time:

$$\frac{\Delta \rho_i}{\Delta t_i} = -\mu_0 V_i, \tag{1}$$

where μ_0—is the initial concentration of biomass;;

$\Delta \rho_i = \rho_i + 1 - \rho_i$—concentration increment;

$\Delta t_i = t_i + 1 - t_i$—time increment;

V_i—specific oxidation rate.

For V_i values, it should be understood as the average values of the specific velocity in the interval $\Delta \rho \acute{\iota}$ interact with the average values of the concentration in the same interval. The statistical significance of the curves of the "specific rate-concentration" type shows a functional dependence with a maximum [5]. The kinetic model is derived from the parametrization of experimental data rather than from theories explaining the results of the observed parameters.

The parameters received:

1. Interaction of the elements ammonium and phosphorus with microorganisms, without which biochemical the process is not possible.
2. The influence of the environment on the ability of microorganisms to decompose, which is determined by the concentration of ammonium and phosphates in wastewater.

The first parameter is determined by the power law depending on concentration. The second parameter is the distribution oxidation rate with increasing substrate

Table 1 Results of experimental data

№	Filtration rate, l / h	Before processing, after Tue. sedimentation tanks, mg / l		After processing on a biofilter, mg / l		Vi is the specific oxidation rate	
		Ammonium	Phosphates	Ammonium	Phosphates	Ammonium	Phosphates
1	0.4	2.53	2.51	2.45	1.46	2.33	12.86
2	0.8	2.53	2.51	2.38	1.27	2.15	7.03
3	1.2	2.53	2.51	2.5	0.92	2.45	5.42
4	1.6	2.72	1.32	2.52	1.33	2.18	0.82
5	2	2.72	1.32	2.21	1.28	1.33	0.69

concentration. The coefficient taking into account this dependence is equal to unity at zero concentration of substances tending to zero with increasing pollutant. With this coefficient, we obtain the dependence [6]:

$$V_{\rho} = \alpha \cdot \rho^{b} \cdot e^{-c\rho}, \tag{2}$$

where a, b, c—empirical coefficients;

$V\rho$—dependence of the specific oxidation rate on the concentration of the pollutant, l/h;

ρ—concentration of a pollutant, g / m^3;

e—constant = 2718.

Finding empirical coefficients is straightforward. Taking the logarithm of formula (2) and replacing the variables, we obtain the linear regression equation, the definition of which is possible using data analysis, the regression function in EXCEL.

This dependence (2) is necessary, but insufficient for calculating the stationary process of biochemical destruction [7].

When passing from expression (1) at $\Delta t \to 0$, we obtain an equation describing the process of biochemical purification in differential form:

$$\frac{\partial \rho}{\partial t} = -\mu_0 V, \tag{3}$$

where ρ—is the increase in the concentration of the pollutant;

t—is the time increment;

V—specific rate of oxidation.

Expression (3) describes the kinetics of the biochemical oxidation process, where the dependence of the pollution concentration on time is the specific rate. The kinetic model of biochemical oxidation is a system of two functions showing the interaction the concentration of the removed substance in the time of the cleaning process, obtained on the basis of interaction of the same parameters in differential form:

$$\rho = f_p(t);\ V = f_v(\rho). \tag{4}$$

where f—is the antiderivative function.

The results of statistical processing are shown in Fig. 2 and in Table 2. The form of the dependence for V adequately describes the experimental model. The obtained data of biochemical purification from ammonium and phosphates are statistically significant according to the F criterion and the coefficient of determination. Thus, the proposed dependence (2) is a universal kinetic model of biochemical destruction [6].

The minimum coefficient of determination was $R_2 = 0056$.

The resulting kinetic model is universal for calculating specific, non-stationary processes in biofilters.

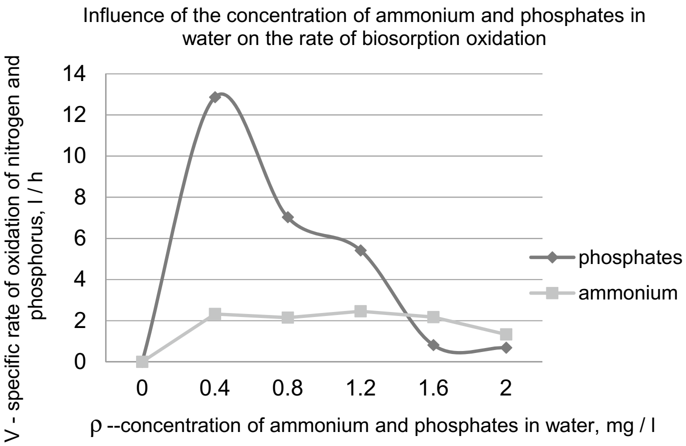


Fig. 2 Influence of the concentration of ammonium and phosphates in water on the ate of biosorption oxidation

Table 2 Results of statistical processing of experimental data for relationships of the form "specific rate—concentration"

V—function, ρ- argument	Regression equation coefficients			Confidence interval of deviations of the regression equation from the experiment	Determination coefficient, R_2	The ratio of the calculated value of the F-criterion to the table
	a	b	c			
V—specific rate of nitrogen oxidation, l / h	2.514	0.136	0.001	0.130	0.184	0.678
ρ- ammonium concentration in water, mg / l	2.514	0.136	0.001	0.130	0.184	0.678
V—specific rate of phosphorus oxidation, l / h	1.342	0.235	0.011	0.225	0.056	0.178
ρ- concentration of phosphates in water, mg / l	1.342	0.235	0.011	0.225	0.056	0.178

According to the data obtained, the efficiency of destruction was obtained.

It was revealed that the efficiency of additional purification of wastewater from biogenic elements by a filmless slow filter in relation to ammonium is 63.3%, in relation to phosphates—18.8%.

4 Conclusions

1. The parameters of the dependence of the oxidation rate on concentration of harmful substances, the contact of ammonium and phosphates with microorganisms was determined, without which the biochemical process is impossible. Obviously, the depressing effect of the environment on the ability of microorganisms to decompose.
2. A kinetic model of the biochemical oxidation process has been built, showing a system of two functions that determine the dependence of the concentration of the removed substance in time.
3. The efficiency of additional purification from ammonium by 18.8% and phosphates by 63.3% was obtained, which made it possible to reduce the concentration of ammonium and phosphates below the established norms of discharges of harmful substances.

Acknowledgements The reported study was funded by RFBR according to the research project № 20-38-90004.

References

1. Ulchenko VM (2010) Post-treatment of waste water on filters with granular loading. Water Supply and San Technics 12(C):34–38
2. Pervov A, Spitsov D (2011) Application of membrane techniques for municipal wastewater treatment and reuse. Inżynieria Ekologiczna 24(P):107–119
3. Veza JM (26–27 Apr 2004) Water desalination and wastewater reuse for agriculture in Spain. Proceedings of the fao expert consultation on water desalination for agricultural applications, Rome P, 19–28
4. Golovin VL (2011) Tertiary waste water treatment. Problems of land reclamation and water management in the Far East of Russia Sat scientific works of DalNIIGiM. Vladivostok, Dalnauka, 17(P), 155–173
5. Krichkovska LV, Vaskovets LA, Gurenko IV (ed) (2014) iн—Kharkiv design solutions for the development of biological devices for biological purification of gas-like wikids. NTU "KhPI",. p 208
6. Bakharava GY et al. (2015) Development of macrokinetic models for the process of biological purification of gas accumulated sums. Sci Rise 2(7). S:12–15
7. Bakhareva AY et al (2016) Development of a universal model of the kinetics of the stationary process of biological purification with sub-stranded inhibition. Eastern Euro J Adv Technol 2/10(80), 19–26