DEVELOPMENT OF THE MATHEMATICAL MODEL OF THE KINETICS OF THE STATIONARY PROCESS OF BIO-CLEANING WITH SUBSTRATIC INHIBITION

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Abstract: A scientifically sound method for calculating the parameters of bio-cleaning should contain as a basic a reliable mathematical description of the stationary process. The results of stationary laboratory experiments are presented in the coordinates "specific rate of destruction V – concentration ρ". Statistical processing proves the presence of substrate inhibition for both gaseous and soluble and dissolved harmful substances in water. For an analytical description of the dependence of the biooxidation rate on the concentration of contaminants, a phenomenological approach is applied, taking into account in a simple form two obvious phenomena: the contact of a microorganism with a substrate molecule and the inhibitory effect of the medium on it. The numerical values of empirical dependency coefficients for the studied processes are calculated.
A differential equation is proposed at the macro level that describes the kinetics of biochemical destruction. The concept of a macrokinetic mathematical model of bioremediation is defined as a system of two functions that quantitatively reflect the dependence of the specific oxidation rate of pollution on its concentration and concentration on time, as well as satisfying the relationship between the relationships of the same parameters in differential form. The dependence of concentration on time is defined both in the form of a numerical integration algorithm and in the form of an approximate formula. The adequacy and universality of the proposed model for the studied processes is proved. The advantage of the proposed model of substrate inhibition kinetics is the simplicity of the structure of the basic formula and the ease of determining empirical coefficients based on this. In addition to numerical integration for determining the time of destruction, an approximate analytical solution is found, which can be adequately used in the concentration range of the experimental study. Further research is aimed at developing methods for calculating non-stationary processes in biochemical purification plants of certain specific types.
Keywords: biochemical destruction, substrate inhibition, phenomenological approach, macrokinetic model, specific oxidation rate, pollution concentration.

1. Introduction

High environmental friendliness, efficiency and versatility of biotechnological methods of purification of industrial pollution determine their prospects in the field of environmental protection. Today, methods of biological purification of gases, such as bioabsorption and biofiltration, are of particular interest in relation to the destruction of a wide range of organic and inorganic pollutants [1]. Numerous scientific publications have reviewed the possibility of purifying gases from ammonia, hydrocarbons, hydrogen sulfide, ethyl mercoptan, carbon disulfide [2], dimethyl sulfide, ethanol, benzene, toluene [3], ethyl benzene, formaldehyde, dichloromethane, and other substances [2–4]. Bioreactors of various designs are applicable for cleaning, for example, bioscrubbers and bioabsorbers [5], reactors with a washable bed [6], membrane bioreactors [7], biofilters with different filling [8], for example, soil [9]. Quite a lot of work is devoted to the description of the mechanisms that occur during biological detoxification of emissions. For example, in [10], the kinetic characteristics of the process of destruction in a biofilm of gas cleaning devices are considered. According to the results of production data [11], the parameters of the kinetics of hydrogen sulfide removal are determined. Mathematical descriptions of the processes in the irrigated biofilter are performed, based on a statistical method for evaluating experimental data [12] and on the idea of mass transfer [13, 14].

At the same time, the design of processes for the biochemical destruction of harmful substances requires the development of scientifically based calculation methods.

The processes of biochemical detoxification, which are realized in bioreactors and plants of periodic action, are non-stationary due to external influence. External impact on the reaction zone is expressed in the form of receipt and removal of a harmful substance, as well as in the form of a change in its volume. Thus, an adequate mathematical description of a non-stationary process will be a superposition of a mathematical model of a stationary process and a combination of external influences characteristic of this particular installation. Obviously, a scientifically based method for calculating and designing a bioremediation process as its main component should contain a common part – a mathematical description of a stationary process.

2. Methods

The kinetics modeling technique is based on previously conducted experimental studies of stationary processes of biooxidation of gaseous harmful substances dissolved [15] and not soluble in water [16], as well as contaminations dissolved in water [17]. Equipment and experimental conditions are described in [14–18]. In these works, stationary processes of biochemical destruction were modeled without additional supply of the pollutant during the experiment (a bioreactor of periodic action). The primary results of the experiment were points in the coordinates "concentration ρ – time t". Each point was averaged over three to five values. For direct statistical processing, the initial experimental data were presented in the coordinates "specific rate of destruction V – concentration ρ". The regression dependence was found using the LINEST program in EXCELL. Mathematical modeling was based on a phenomenological approach using classical concepts of the kinetics of the process with substrate inhibition.

3. Results

The theoretical basis for the description of bio-cleaning processes is the laws of biological kinetics, which are the most important part of research in biophysics. Biological kinetics models mathematically describe enzymatic reactions of various types. To date, various reaction mechanisms have been considered, the most famous and simplest of which is the classical Michaelis-Menten model [19, 20]. At the same time, the practical application of mathematical models of biophysics is not without certain difficulties and shortcomings. Mathematical models are systems of differential equations, simplified as a result of

the assumption that the enzymatic act is stationary, to systems of ordinary linear equations. The solution of these systems is always a fractional function, for the practical use of which it is necessary to determine the kinetic coefficients by comparing the calculation formula with the laboratory experimental data [21]. The structure of the models (fractional function) does not allow to obtain reliable values of coefficients directly by a graphic method. Therefore, in practice, the transition to a system with inverse coordinates is used. In the case of substrate inhibition, substantial assumptions are introduced that reduce the initial dependence to the Mono formula for low and to the hyperbole for high concentrations [19, 20]. Direct statistical calculation also inevitably leads to a distortion of the actual values of the coefficients due to the use of a system with inverse coordinates [22]. In addition, with a previously unknown maximum order of an unproductive enzyme-substrate complex, the influence of already the fourth complex may not be captured due to the error of the initial data. Therefore, taking into account in the research calculations of the complex mechanism of substrate inhibition can be offset by the inaccuracy of quantitative estimation of the parameters of formulas and the uncertainty of laboratory experiments.

The foregoing demonstrates the legitimacy of using in practical calculations an approach in which the deliberate coarsening of a mathematical description of the reaction mechanism using averaged parameters makes it possible to reliably determine empirical coefficients. This approach is phenomenological and is based on chemical kinetics [23, 24]. Phenomenological models are derived from the successful parameterization of experimental data, and are not derived from theories with a detailed explanation of the mechanism of the observed phenomena. In chemical kinetics, the average concentration is used, and the actual reaction mechanism is taken into account only by its order [19, 20].

In the case of substrate inhibition, the following phenomena are evident:

1. Contact of a pollutant molecule with a microorganism, without which a biochemical process is impossible.

2. The inhibitory effect of the environment on the ability of a microorganism to biodegrade, determined by the concentration of a harmful substance.

The effect of the first phenomenon, as in chemical kinetics, can be estimated by a power dependence on concentration. The content of the second phenomenon is the relaxation of the specific oxidation rate with increasing substrate concentration. The coefficient taking into account its influence will be equal to unity at zero concentration of the pollutant, and tend to zero when it increases. In the most general form, this corresponds to an exponential curve that implements the effect of inhibition at any power dependence on concentration. Thus, adding a scale factor, let's obtain the dependence of the specific rate of destruction on the concentration of the pollutant [25]:

$$V_\rho = a \cdot \rho^b \cdot e^{-c\rho}, \quad (1)$$

where a, b, c – empirical coefficients.

At the same time, finding empirical coefficients is not difficult. Having transcribed expression (1) and replacing the variables, let's obtain a linear multiple regression equation, the determination of the coefficients of which is not difficult. The results of statistical processing prove that the proposed type of dependence for V adequately describes the experimental data [26]. The obtained regression formulas for all the studied processes of biochemical purification are statistically significant by the F-criterion and coefficient of determination R^2. Thus, the proposed dependence (1) is a universal component of the macrokinetic model of the biochemical destruction of methane, ammonia, hydrogen sulfide, sulfur dioxide and formaldehyde.

The obtained dependence (1) is necessary, but not sufficient for practical calculations of the stationary process of biochemical destruction. At the macro level, the kinetics of the biooxidation process describes a differential equation:

$$\frac{d\rho}{dt} = -\mu_0 V, \quad (2)$$

where μ_0 – the initial biomass concentration.

Its decision, with a known specific speed, will be the dependence of the concentration of pollution on time, which is missing to a complete description of the process. Thus, the macrokinetic mathematical model of biochemical purification is a system of two functions, quantitatively reflecting the interdependence of the concentration of the removed substance, the duration of the purification process, the specific rate of destruction of the harmful substance and the initial concentration of biomass, obtained on the basis of the interrelation of these parameters in differential form.

The exact solution of equation (2) using expression (1) is impossible. Therefore, for a certain integral, let's use numerical integration, in which at each i-th step replace the exact value of the velocity with a linear approximation and, after transformations, obtain formulas for calculating the concentration increments at each i-th step of numerical integration. In addition, the possibility of obtaining an approximate analytical solution is realized by replacing the known integral inequality with equality. After integration and transformations:

$$t = m(\rho_0^n - \rho^n) e^{\frac{p(\rho_0^{n+1} - \rho^{n+1})}{\rho_0^n - \rho^n}}, \quad (3)$$

$$m = \frac{1}{\mu_0 a(1-b)}; \quad n = 1-b; \quad p = c\frac{1-b}{2-b}, \quad (4)$$

where t – the time required to reduce the concentration of a harmful substance from ρ_0 to ρ.

The results of calculations using formula (3) show high statistical significance both in relation to the experimental data and in accordance with the results of numerical integration. The minimum coefficient of determination is R^2=0.9918.

4. Discussion

The regression equation of the form (2) and the interrelated formula (3) together constitute a macrokinetic mathematical model of the biochemical oxidation process with substrate inhibition. The adequacy and universality of the developed model for the studied spectrum of destructible harmful substances has been proved.

The advantage of the proposed model of substrate inhibition kinetics is the ease of determining empirical coefficients, based on the obvious physical meaning of the structure of the basic formula. The disadvantages of the model include an approximate analytical solution for determining the time of destruction, the adequate use of which is possible in the range of concentrations of the experimental study. Further research includes the development of methods for calculating non-stationary processes in biochemical purification plants of certain specific types.

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