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DEVELOPMENT OF A PHENOMENOLOGICAL MODEL OF THE KINETICS OF BACTERIAL ADSORPTION ON LOW-ENERGY SURFACES

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A mathematical model of the kinetics of bacterial adsorption on polymeric materials with various hydrophobicity is developed. The model describing the bacteria-liquid phase-polymer surface system is capable of predicting the amount of bacteria adsorbed on the surface within a certain period of time. The model is based on the resolution of the motive force of adsorption into two components. The first component characterizes the interactions based on the hydrophobic properties of bacteria and polymers and is expressed in terms of interphase tensions. The second component describes the remaining types of interactions, which cannot be represented in a similar way.

Our work was dedicated to the establishment of a quantitative relation between the rate of adsorption of a certain class of microorganisms on polymeric materials and their adhesion to the latter. The results of an analysis of the free energy of adhesion of microorganisms to various polymeric materials and the experimentally found amounts of microorganisms adsorbed on polymers per unit time [1] are a direct corroboration of the existence of this relation.

The simplest physicochemical approach widely employed in describing the adhesion process is the one based on classical thermodynamics [2]. At present, this approach is extensively used in many works to describe the bacterial adhesion process [1, 3-6]. Based on these papers, we may conclude that two main factors affect the adhesion process: the hydrophobicity of the bacterial wall and the adsorbing surface on the one hand and their charges, on the other.

In some special problems concerning granulation processes and the development of biofilms, the key factor is the rate of bacterial adsorption. Various attempts have been made in this field [7, 8]. As a rule, these works deal with the time dependence of the number of bacteria adsorbed on unit area determined by statistical methods. However, no description of the kinetics of this process in terms of energy parameters, as, for example, in the Arrhenius law for the kinetics of a chemical reaction, has been made until now.

One of the possibilities for finding this relationship resides in representing the rate of the adsorption process as a sum of the rates of processes having different origin. In this case the kinetics of bacterial adsorption can partly be expressed on the basis of thermodynamic propositions. A similar approach was used for establishing the relationship between the free energy of adhesion and the number of adsorbed bacteria [9, 10]. Unfortunately, the resultant relationships describe only the final equilibrium states of the liquid-bacteria-adsorbing surface system; it is not possible to obtain any expressions for the kinetics of the process. Nevertheless, it is clear that this approach may be useful in the development of the fundamentals of the kinetics.

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In this article we consider adsorption of hydrophilic microorganisms on low-energy uncharged surfaces. In this case, we may expect that the motive force of the adsorption process is based on hydrophobic interactions. Moreover, the well-known equation of state for calculating the adhesion energy in terms of surface tensions can be employed in the analysis of the kinetics of bacterial adsorption.

The choice of the system in question is not accidental. As was shown [11], it is not always possible to find a clear-cut correlation between the electrophoretic mobility of bacteria and their adhesion to materials with different surface properties. Thus, by selecting the required experimental conditions, we may expect that the contribution of electrostatic interactions will be low. The contribution of other interactions (including electrostatic) to the adhesion process can be taken into account by using an additional parameter.

THE DEVELOPMENT OF A MODEL

The main dependences of the model describing the number of bacteria adsorbed on unit surface as a function of time are represented by Eqs. (1) and (3). Because in the present paper we consider short-duration experiments, the bacterial growth on the surfaces of materials is not taken into account.

$$\frac{dN}{dt} = \phi_1 N_{\text{ext}} [\exp(-\phi_2 \Delta G_h(t)) - 1 + \Psi] \frac{S^{\text{access}}(t)}{S^{\text{tot}}}, \quad \Delta G_h \leq 0, \quad (1)$$

$$\frac{dN}{dt} = \phi_1 N_{\text{ext}} \Psi \frac{S^{\text{access}}(t)}{S^{\text{tot}}}, \quad \Delta G_h > 0, \quad (2)$$

$$S^{\text{access}}(t) = S^{\text{tot}}(1 - N(t)S^{\text{tot}}). \quad (3)$$

As is seen in Eq. (1), the rate of bacterial adsorption is represented by the sum of two terms. The first term containing ΔG_h is the rate of adsorption determined by the hydrophobic properties of the wall of the bacterial cell and of the surface of the material. It is expressed through interphase tensions (type 1 interaction). Ψ in Eqs. (1) and (2) describes the contribution of other interaction types to the process of adsorption (type 2 interaction). For this reason, the $\Delta G_h > 0$ condition in Eq. (2) denotes the zero contribution of the hydrophobic component to the adsorption process.

It is also assumed that the adsorption rate is directly proportional to the number of cells in unit volume of the surroundings, N_{ext} , and to the portion of the surface $\{S(t)\}/S$ that is accessible for the adsorption process. The absolute value of the accessible surface at any time is calculated from Eq. (3). The use of the resolution of motive forces of this type makes it possible to analyze both terms in the rate expressions independently of one another.

It follows from thermodynamics that if only hydrophobic properties are to be analyzed, the process of bacterial adhesion will depend on the changes in the so-called free energy of adhesion or Gibbs' free energy (ΔG_h) between the following phases: solid-liquid, bacterium-solid, and liquid-vapor. In this case the adhesion process occurs if the adhesion energy of the system becomes lower. This energy can be found from Eq. (4).

One of the main ideas of our work consists in the use of ΔG_h for the description of the contribution of hydrophobic interactions to the adsorption process. In order to calculate the ΔG_h value, Eq. (4) should be supplemented by Eqs. (5)–(8). Equations (5) and (7) are the Young equations [2] for two systems: one system includes the surface of the polymer, liquid, and vapor, the second, the wall of the bacterial cell, liquid, and vapor. Using the equation of state [12, 13], we can supplement Eq. (5) with Eq. (6). This makes it possible to find in a unique fashion γ_{LV} (and γ_{SL}) if the experimental data on the wetting angle Θ_{SL} and on the surface tension of the liquid γ_{LV} are known. Moreover, Eqs. (5) and (6) allow one to find γ_{SL} for any value of the surface tension of the liquid based on the γ_{SV} value found earlier,

$$\Delta G_h = \gamma_{BS} - \gamma_{BL} - \gamma_{SL}, \quad (4)$$

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \Theta_{SL}, \quad (5)$$

$$\cos \Theta_{SL} = -1 + 2 \sqrt{\frac{\gamma_{SV}}{\gamma_{LV}}} \exp(-0.0001247(\gamma_{LV} - \gamma_{SV})^2). \quad (6)$$

A similar approach can be used in finding γ_{BV} (and γ_{BL}) from Eqs. (7) and (8) on the condition that the experiment gives the values of the wetting angle Θ_{BL} and of the surface tension of the liquid γ_{LV} . In this case Eqs. (7) and (8) are used for determining γ_{BL} for any γ_{LV} value from the γ_{BV} value found above,

$$\gamma_{BV} - \gamma_{BL} = \gamma_{LV} \cos \Theta_{BL}, \quad (7)$$

$$\cos \Theta_{BL} = -1 + 2\sqrt{\frac{\gamma_{BV}}{\gamma_{LV}}} \exp(-0.0001247(\gamma_{LV} - \gamma_{BV})^2). \quad (8)$$

Formally, the equation of state can be applied to calculate $\cos \Theta_{BS}$ from γ_{SV} and γ_{BV} . Using the Young equation and the hypothetic value of the wetting angle, we can find γ_{BS} .

Thus, Eqs. (4)–(8) allow us to calculate the changes in the adhesion energy between two states for an individual bacterium in the case where only hydrophobic interactions are taken into account. It should be noted that in the present work we used a new form of the relationship between the experimental values of the wetting angle and of the surface tension (Eqs. (6) and (8)). The main advantage of this form, which was derived earlier [13], is the absence of singularity in the equation for the wetting angle.

The process of bacterial accumulation on the surface of an inert material leads to a change in the averaged hydrophobic properties of the adsorbing surface. This fact can be taken into account by introducing the effective wetting angle $\Theta_{SL}^{\text{eff}}(t)$, which can be measured experimentally. As was shown earlier [14], the hydrophobicity of a bacterial mixture is the average of the hydrophobicities of its components. Using this fact, we can calculate the effective hydrophobicity of the surface of the material as the average of the hydrophobicities of the portion that is occupied by the bacteria $(1 - S(t)/S)$ and the portion that is free from the latter $(S(t)/S)$, respectively,

$$\cos \Theta_{SL}^{\text{eff}}(t) = \left(1 - \frac{S(t)}{S}\right) \cos \Theta_{BL} + \frac{S(t)}{S} \cos \Theta_{SL}. \quad (9)$$

As the surface is covered with bacteria, the $\cos \Theta_{SL}^{\text{eff}}(t)$ function approaches in time the constant value Θ_{BL} . In our work the Θ_{SL} value, which depends only on the properties of the surface and liquid, will be used for calculating the ΔG_h value. This means that the bacteria will be fixed on the free portion of the surface rather than on bacteria adsorbed earlier; hence, the free energy of adhesion will remain unchanged. Nevertheless, the rate of adsorption will decrease as the available area is reduced.

Equations (4)–(8) are all that is necessary for calculating the first component of the adsorption rate based on the hydrophobic properties of the wall of the bacterial cell and on the properties of the surface of the inert material (type 1 interactions).

The second term in Eqs. (1) and (2), Ψ , characterizing the contribution of type 2 interactions to the adsorption rate can be determined from Eq. (2). In this case the rate of adsorption does not depend on ΔG_h . As in the present paper we consider adhesion to low-energy surfaces, the contribution made by the Ψ value may be assumed to be sufficiently low. Thus, if the experiment is designed in such a manner that it contains the area where $\Delta G_h > 0$, the Ψ term can be determined experimentally.

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