Kinetics of the Enzymatic Decomposition of Macromolecules with a Fractal Structure

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Abstract—Mechanisms of enzymatic decomposition of an organic substance consisting of fractal macromolecules of different sizes are studied. A kinetic decomposition equation in which the reaction rate coefficient depends on the characteristic of the fractal structure is formulated. The solution for a fraction of macromolecules of the same size and for a mixture of macromolecules of different sizes is analyzed. It is shown that the decomposition kinetics depends on the fractal structure of the macromolecules and the type of their initial distribution by size. Conditions under which the decrease in the concentration of the organic substance obeys the power law are found. The theoretical relations are used for analyzing the literature data on the decomposition kinetics of organic matter in sea sediments in the time interval from several hours to about one million years. It is shown that in this whole interval the concentration decreases with time according to the universal power law with a 0.14 exponent. The kinetics of enzymatic decomposition of lignin (product of the natural decomposition of plant remains or byproduct of wood processing) is also discussed. It is found that the exponent accounting for the concentration decrease is equal to 0.4 to 0.5 for the decomposition of industrial lignin in bulk water and 1 to 2 for its decomposition in the water with bottom sediments.

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Study of the decomposition of organic matter in natural water ecosystems and industrial processes such as the processing of wood and wastewater treatment is of current concern to the solution of environmental protection problems.

The basic hard-to-oxidize components of organic matter in natural water are lignin and products of its transformation, including humic and tannic substances, phenols, quinones, and the like [1, 2]. The natural way of their supply is the rain surface runoff bringing plant remains and the products of their decomposition. A part of these substances will later get decomposed in the bulk water whereas the most stable of them will adsorb on the suspended particles and settle down with the particles to bottom sediments, where the matter that did not have enough time to get mineralized will be buried under the sediment layer [3]. At the largest scale, this process proceeds in the world ocean and makes a significant contribution into the balance of carbon on the planet [4]. To more accurately identify the flows of substances containing carbon, it is necessary to more thoroughly study the decomposition kinetics of organic matter.

Industrial effluents are the alternative way of the supply of hard-to-oxidize organic matter. This way is a serious danger to the natural water environment. One of the leading places regarding the volumes of consumed water and wastewater effluents is taken by the pulp-and-paper industry. Its effluents bring large amounts of lignin and its derivatives to water ecosystems [5]. Lig-

nin is hard to remove during the wastewater treatment. Most of it passes through the treatment equipment without any change [6]. Consequently, it is important to estimate the self-treatment potential of the natural water exposed to such high technogenic loads [7]. The study of the decomposition kinetics of lignin will allow us to advance in this direction.

Lignin is a typical representative of a wide class of technogenic and natural organic macromolecules. As it is rather well studied, it can be considered as an example to study the enzymatic decomposition of a stable organic. Therefore, the modern concepts about the structure and decomposition mechanisms of lignin will be briefly discussed below in order to use this information in formulating the ideas on which the model to be developed will be based.

Lignin is a natural polymer, which is one of the main components of wood. It is produced by the polycondensation of phenylpropane monomer chains, which can exist in different mesomer forms [8]. The variety of primary structures lead to heterogeneity and chaos at the macromolecular level [9]. The topological structure of lignin macromolecules is dendroidal (a tree graph) [10] with rare intermolecular ties (rings) [11]. In wood, the lignin exists as a gel-like boundless net. In water, it exists as a sol with a wide spectrum of the sizes and structures of macromolecular clusters [12–15]. In the synthesis of lignin, the limiting factor in the formation of clusters is diffusion. Because of the high reactivity of phenoxyl radicals, the polymerization proceeds by the

following patterns: random attachment of phenylpropane chains to already existing growing macromolecules for low monomer concentrations and cluster–cluster aggregation for high monomer concentrations [16, 17]. It is assumed that in the synthesis of lignin the reactivity of functional groups is independent of the size and complexity of macromolecules (Flory's principle [18]). It is well known that either growth mechanism gives rise to fractal clusters, though their fractal dimensions are different [19]. According to estimates [20, 21], the fractal dimension of dioxane lignin and lignosulfonate macromolecules is 2.44. According to the modern physical theory, this value corresponds to particle–cluster aggregation. Indeed, the numerical simulation of aggregation in this case leads to a dimension of 2.5 whereas the cluster–cluster growth mechanism produces less dense aggregates with a dimension of 1.8 [19, 22].

In the nature, lignin is decomposed by specific enzymes discharged by various fungi and bacteria [23–27]. The lignin-decomposing group includes fungi of white rot. They secrete lignolytic enzymes such as laccase, peroxidase, and tyrosinase, which can act outside the cell, decomposing lignin macromolecules to dissoluble products that can diffuse through the cell membrane inside the cell. Most enzymes discharged by fungi produce a combined action: hydrolysis, oxidation, tie cleavage, and detachment of functional groups. The lignolytic ability of bacteria in most cases is much lower than that for fungi [28].

The mechanisms of the catalytic action of enzymes are well studied for low-molecular substrates [29–31]. In this case, a small substrate molecule adsorbs on the active site of the molecule of an enzyme, is transformed into a product molecule, and desorbs from the enzyme. Remember that a large protein molecule folded into a compact globule is the base of an enzyme.

A different situation is for lignin macromolecules, which are much larger than the molecules of an enzyme. In this case, the substrate molecule itself adsorbs enzymes on its surface and does not let them enter into its body because of the steric limitations. The enzymes decompose the lignin macromolecule by detaching small fragments from its surface. Later, these fragments are involved in the metabolism of microorganisms [28], where the regular mechanisms of enzymatic catalysis act. The detachment rate of fragments is independent of the size and complexity of the macromolecules, which corresponds to the mentioned Flory principle.

When the decomposition degree of lignin is determined by experiment, different parameters accounting for the content of organic matter (chemical oxygen demand, optical indices such as color index), which are directly or indirectly related to the total content of organic carbon concentrated in the lignin molecules [5, 6]. Therefore, when the decomposition kinetics of lignin is theoretically described, it is necessary to ulti-mately obtain the dependence of the concentration of organic carbon on time.

In the present paper, we will develop a kinetic model for the enzymatic decomposition of organic matter, using lignin as an example and the well-known concepts about its structure and decomposition mechanisms.

DECOMPOSITION KINETICS

Summarizing the above, we can formulate the following main principles that will be used in simulating the decomposition kinetics of lignin:

(1) Lignin is a mixture of macromolecules with a wide spectrum of sizes and structures.

(2) The topological structure of lignin macromolecules possesses fractal properties.

(3) Lignin is decomposed with the help of enzymes by detaching its small fragments from the surface of the macromolecules. The detachment rate of one fragment is independent of the size and complexity of the macromolecule.

These principles are true not only for lignin but also for other organic substances in which the macromolecules are produced by the polycondensation of certain structural units, such as humic substances, which are much common in soil and water. That is why our theoretical consideration will be based on organic molecules of the indicated class. In the present paper, we will formulate the simplest (basic) model of the process in which the fluctuations of the medium properties are assumed to be very weak.

Consider the variation of the number of carbon atoms in the molecules of an organic substance when they are enzymatically decomposed. Simplifying the actual situation, we assume that only the same fragments are detached from the surface of macromolecules (for example, phenylpropane monomers, which are the structural units of lignin). In this case, the pattern of the sequential detachment of fragments from the surface of macromolecules can be written as

$$\ldots \longrightarrow (n+1) \xrightarrow{k_{n+1}} (n) \xrightarrow{k_n} (n-1) \longrightarrow \ldots, \quad (1)$$
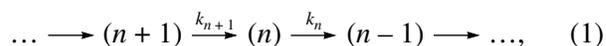
where (n) is the molecule of dimension n (that is, the one consisting of n structural units).

Let N_n denote the molar concentration of molecules of dimension n. According to reaction (1), the rate of change of the concentration of these molecules is written as

$$dN_n/dt = k_{n+1}N_{n+1} - k_n N_n. \quad (2)$$

As $n \gg 1$ for macromolecules, we can transfer from the discrete description to continuous by introducing a distribution density instead of the concentration N_n. By definition, $f(n)$ is the molar concentration of molecules

with dimensions in the range $(n, n + dn)$, Instead of (2), we come to the equation:

$$\frac{\partial f}{\partial t} = \frac{\partial k(n) f}{\partial n}, \tag{3}$$

where $k(n) \equiv k_n$ and $f = f(n, t)$. Equation (3) should be complemented by the initial condition:

$$t = 0, \quad f = f_0(n). \tag{4}$$

Equation (3) can be solved by the method of characteristics:

$$dt = -\frac{dn}{k(n)} = \frac{df}{k'(n) f}.$$

The first integrals are written as

$$t + \int \frac{dn}{k(n)} = C_1, \quad k(n) f = C_2. \tag{5}$$

The function $k(n)$ can be found from the following consideration:

As the decomposition occurs on the surface of the macromolecule, the rate of an elementary fragment-detachment reaction is proportional to the probability at which the enzyme can occur on the surface. The latter in turn is proportional to the surface area of the macromolecule S; that is, $k \sim S$. As indicated above, the macromolecule is characterized by fractal properties. It is well known that the volume V and surface S of a fractal aggregate can be written in terms of its radius as $V \sim R^d$ and $S \sim R^D$, where d and D are the fractal dimensions of the aggregate and its surface [19], which can vary in the intervals $d \in [1, 3]$ and $D \in [2, 3]$. As the volume is proportional to n, $n \sim R^d$. It follows from these relations that $R \sim n^{1/d}$ and $S \sim n^{D/d}$. This gives us the desired relation:

$$k(n) = k_1 n^{\nu}, \tag{6}$$

where $\nu = D/d$ is the fractal index of the molecule, which varies in the interval $\nu \in [2/3, 3]$.

Now return to formulas (5). Using the found relation for $k(n)$, we obtain

when $\nu \neq 1$: $(1 - \nu) k_1 t + n^{1 - \nu} = C_1, \quad n^{\nu} f = C_2$, (7)

when $\nu = 1$: $k_1 t + \ln n = C_1, \quad n f = C_2$ (8)

Here, the additive constants C_1 and C_2 are differently defined as compared to (5). Equations (7) and (8), and initial condition (4) yield the following relations:

$$C_2 = C_1^{\nu/(1 - \nu)} f_0(C_1^{1/(1 - \nu)}), \quad \nu \neq 1,$$

$$C_2 = e^{C_1} f_0(e^{C_1}), \quad \nu = 1.$$

Substituting expressions (7) and (8) for C_1 and C_2 in the above relations, we obtain

$$f = \left(\frac{z(n)}{n}\right)^{\nu} f_0(z(n)),$$

$$z(n) = (n^{1 - \nu} + (1 - \nu) k_1 t)^{1/(1 - \nu)}, \quad \nu \neq 1. \tag{9}$$

$$f = e^{k_1 t} f_0(n e^{k_1 t}), \quad \nu = 1. \tag{10}$$

When distributions (9) and (10) are known, we can find the concentration of structural units in the molecules that are not decomposed yet:

$$c = \int_0^{\infty} n f(n) dn. \tag{11}$$

It is obvious that the concentration of organic carbon is proportional to this quantity (more correctly, it is equal to $n_1 c$, where n_1 is the number of carbon atoms in one structural unit). Consequently, the equations for the concentration c to be derived below can be interpreted as the equations for the concentration of organic carbon when the parameters are appropriately renormalized.

DECOMPOSITION OF A UNIFORM FRACTION

Assume that the organic substance initially is represented by a uniform fraction made up of macromolecules of the same dimension n_0 with concentration N_0. The corresponding initial distribution has the shape of a delta function:

$$f_0(n) = N_0 \delta(n - n_0).$$

Using the delta-function property [32]:

$$\delta(\varphi(n)) = \sum_i \frac{\delta(n - n_i)}{|\varphi'(n_i)|},$$

where $\varphi(n)$ is an arbitrary differentiable function and n_i are the roots of the equation $\varphi(n) = 0$, distribution (9) can be written as

$$f(n) = N_0 \left(\frac{z(n)}{n}\right)^{\nu} \delta(z(n) - n_0)$$

$$= N_0 \left(\frac{n_0}{n_t}\right)^{\nu} \frac{\delta(n - n_t)}{z'(n_t)}, \tag{12}$$

$$n_t = (n_0^{1 - \nu} - (1 - \nu) k_1 t)^{1/(1 - \nu)}, \quad \nu \neq 1.$$

Substituting distributions (12) and (10) into (11), we obtain

$$c/c_0 = (1 - (1 - \nu) n_0^{\nu - 1} k_1 t)^{1/(1 - \nu)}, \quad \nu \neq 1, \tag{13}$$

$$c/c_0 = e^{-k_1 t}, \quad \nu = 1, \tag{14}$$

where $c_0 = n_0 N_0$ is the initial concentration of structural units.

Equations (13) and (14) can be used to obtain the decomposition kinetics of the organic substance determined by the variation of the total content of organic carbon. To this end, we find the derivative dc/dt and exclude the time from the resulting expression. As a result, we come to the kinetic equation

$$dc/dt = -k_\nu c^\nu, \qquad (15)$$

where $k_\nu = k_1(n_0/c_0)^{\nu-1} = k_1 N_0^{1-\nu}$ is the resultant reaction rate coefficient.

Equation (15) was derived earlier [33] using the multifractional model in the limit of an infinite number of fractions. The derivation proposed in the present paper uses deeper physical principles underlying the mechanism of the process.

In the enzymatic kinetics, there is an analog of Eq. (15), Moser's nonlinear equation [34]:

$$dc/dt = -k_0 c^\nu/(c^\nu + K^\nu), \qquad (16)$$

where k_0 is the decomposition rate constant and K is the half-saturation constant. The equation accounts for the saturation effect at high substrate concentrations. In the nature, the substrate concentration is far from saturation: $c \ll K$. In this case, (16) can be reduced to (15). The Moser equation was initially introduced as semi-empirical. The derivation of Eq. (15) proposed in the present paper can be regarded as the theoretical justification of the nonlinear enzymatic kinetics.

In Eq. (15), the value of $\nu = 1$ corresponds to the first-order kinetics $dc/dt = -k_1 c$ with a characteristic decomposition time $T = 1/k_1$.

For $\nu \neq 1$, the characteristic time T and the exponent ε are introduced using the relationships

$$T = \frac{n_0^{1-\nu}}{|1-\nu|k_1}, \quad \varepsilon = \frac{1}{|1-\nu|}. \qquad (17)$$

The physical meaning of time T can vary depending on whether T is less or greater than unity.

When $\nu < 1$, the concentration of organic carbon decreases by the law

$$c = c_0(1 - t/T)^\varepsilon.$$

In this case, T is the time of the complete decomposition of the organic substance.

When $\nu > 1$, the time dependence of the concentration is written as

$$c = c_0(1 + t/T)^{-\varepsilon}, \qquad (18)$$

where the time T characterizes the duration of the initial stage of the process rather than its whole time. When $t > T$, the decomposition transits to a slow asymptotic stage:

$$c \approx c_0(t/T)^{-\varepsilon}, \qquad (19)$$

which does not have a characteristic time scale and continues endlessly.

DECOMPOSITION OF A MIXTURE

Consider the decomposition kinetics of a mixture with an arbitrary initial distribution of molecules by size. We turn again to formula (11). Assume that $\nu = 1$ and substitute distribution (10) into (11). Simple manipulations give

$$c = c_0 e^{-k_1 t}, \quad \nu = 1,$$

where $c_0 = \int_0^\infty n f_0(n)dn$ by definition. This result coincides with (14). Consequently, the value of $\nu = 1$ provides the reaction first order no matter the initial distribution is.

Now assume that $\nu \neq 1$ and substitute (11) into (9). A set of manipulations yields

$$c = z_t \int_0^\infty [1 + (z_t/z)^{\nu-1}]^{-1/(\nu-1)} f_0(z)dz, \quad \nu > 1, \quad (20)$$

$$c = \int_{z_t}^\infty [1 - (z_t/z)^{1-\nu}]^{1/(1-\nu)} z f_0(z)dz, \quad \nu < 1, \quad (21)$$

where $z_t = (|1-\nu|k_1 t)^{1/(1-\nu)}$.

First consider the $\nu > 1$ case. As $t \longrightarrow \infty$, (20) gives the asymptotic equality:

$$c \approx N_0 z_t = c_0(t/T)^{-\varepsilon}.$$

It completely coincides with (19) if we remember that

$$N_0 = \int_0^\infty f_0(n)dn$$ and the characteristic dimension n_0

involved in formula (17) for the time T is equal to c_0/N_0 by definition.

A power-law asymptotic relationship is also possible for the $\nu < 1$ case. In this case, the initial distribution should have a rapidly descending power-law tail: $f_0(n) \sim n^{-\lambda}$ as $n \longrightarrow \infty$, where $\lambda > 2$. Then, it follows from (21) as $t \longrightarrow \infty$ that

$$c \sim z_t^{-\lambda+2} \sim (k_1 t)^{-b}, \quad b = (\lambda-2)/(1-\nu). \quad (22)$$

The condition $\lambda > 2$ provides the existence of the zeroth and first moments of the initial distribution; that is, the boundness of molecule concentration N_0 and organic carbon concentration c_0 in the initial mixture. The physical reasons for the appearance of the power-law tail of the distribution will be considered later, when the obtained results are discussed.
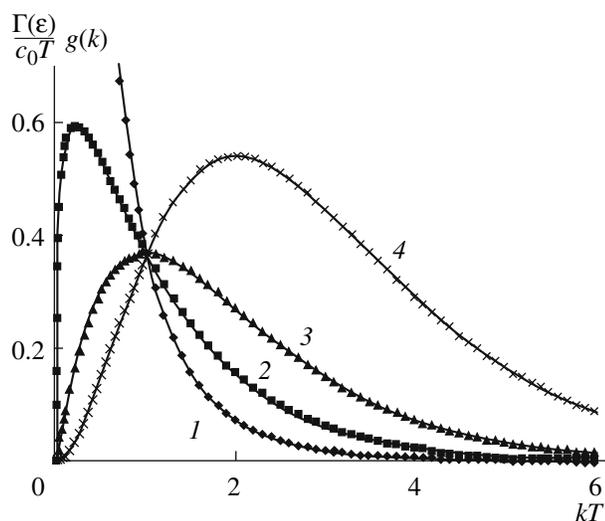
Fig. 1. Spectra of reactivities for ε = (*1*) 0.14, (*2*) 1.2; (*3*) 2, (*4*) 3.

If the initial distribution declines exponentially: $f_0(n) \sim \exp(-n/n_0)$, the concentration will decrease according to the law:

$$c \sim \exp(-z_t/n_0) \sim \exp(-(t/T)^\varepsilon),$$

where $\varepsilon = 1/(1 - \nu) > 1$. This implies that it can decrease slower (when $t < T$) or faster (when $t > T$) than the simple exponential function with $\varepsilon = 1$.

SPECTRUM OF REACTIVITIES

Consider the distribution of molecules over their reactivities. By definition, the reactivity is the decomposition rate constant (coefficient) k in the first-order kinetic equation: $dc_k/dt = -kc_k$,

where c_k is the concentration of molecules with reactivity k.

It follows from this equation that

$$c_k = c_{ok} \cdot 1^{-kt},$$

where c_{ok} is the initial concentration.

For a continuous distribution of molecules by reactivity, it is necessary to consider the density of the distribution by k, which will be denoted by $g(k)$, instead of the concentration. This function specifies the spectrum of the reactivities of organic molecules undergoing enzymatic decomposition. By definition, $g(k)dk$ is the concentration of organic carbon in the fraction of molecules with reactivities found in the interval $(k, k + dk)$. After the decomposition begins, the carbon concentration in this fraction at time t will be equal to $g(k)e^{-kt}dk$

and the total concentration of organic carbon in all fractions will be written as

$$c(t) = \int_0^\infty g(k)e^{-kt}dk. \quad (23)$$

If the spectrum of the reactivities of molecules is known, (23) can be used to calculate the time variation of organic carbon. And vice versa, if the function $c(t)$ is known, the spectrum $g(k)$ can be found. Note that to solve the inverse problem, relation (23) can be regarded as a Laplace transform in which $g(k)$ is the original function and $c(t)$ is its Laplace transform [13]. Using the inverse Laplace transform and the known Laplace transform of some function, we can find this original function. Specifically, when $\nu > 1$, (18) yields the gamma distribution

$$g(k) = \frac{c_0 T}{\Gamma(\varepsilon)}(kT)^{\varepsilon - 1}e^{-kT}, \quad (24)$$

where Γ is the gamma function. Depending on the value of parameter $\nu = 1 + \varepsilon^{-1}$, we obtain spectra of different types (Fig. 1). When $\nu \geq 2$ ($0 < \varepsilon \leq 1$), the spectrum monotonically declines (singularity at zero is integrable). When $1 < \nu < 2$ ($\varepsilon > 1$), the spectrum has a maximum at the point $k = (\varepsilon - 1)/T$.

The distribution of the type (24) has a natural interpretation. In the region of high k ($k > T^{-1}$), the behavior of spectrum (24) is dictated by the exponential function $\exp(-kT)$, which describes the decomposition of the labile fraction during times of the same order of magnitude as T. The behavior of the spectrum in the region of small k ($k < T^{-1}$) is determined by the exponent $k^{\varepsilon - 1}$ describing the decomposition of stable fractions, which requires a higher time for a lower value of k.

When $\nu = 1$, the spectrum is degenerated to $g(k) = (c_0/k_1)\delta(k - k_1)$ (that is, all molecules have the same reactivity $k = k_1$).

ANALYSIS OF EXPERIMENTAL DATA AND DISCUSSION

In testing the adequacy of the model, of high importance are numerous Middelburg's data [35] on the decomposition of organic matter in sea bottom sediments and laboratory experiments, which were gathered from various literature sources. These data cover a uniquely wide time interval: from several hours to about one million years (Fig. 2). In the cited paper, to describe the data, the author proposed a kinetic model of the quasi-first order $dc/dt = -k(t)c$ in which the distinctive feature is the dependence of the decomposition rate "constant" (coefficient) on time. The function $k(t) \sim t^{-a}$ was used. The best agreement was achieved when $a = 0.95 \pm 0.01$. Line *1* in Fig. 2 presents the curve calculated by this model.

Let us estimate the adequacy of the models developed in the present paper. According to them, the decomposition of organic matter can proceed by the power law $c \sim t^{-b}$. The best agreement with measured data is achieved when $b = 0.14$ (Fig. 2, line *2*). It is seen that both approaches, empirical (quasi-first order kinetics) and theoretical (power law), are equally successful in describing the measured data. At the same time, the advantage of the latter is the fact that it is physically grounded.

It should be noted that in one specific case the quasi-first-order kinetics also yields the power-law dependence on time. This takes place when $k(t) \sim t^{-1}$ (that is, when $a = 1$), which is rather close to the found value of $a = 0.95$. Indeed, Middelburg [35] showed that the separation of the data of laboratory experiments, as the most accurate ones, from the whole set of data and their processing give $a = 1.00 \pm 0.06$; that is, the exact value at which both approaches coincide.

Let us turn to estimating the parameters of decomposition kinetics at $b = 0.14$. Assume that $\nu > 1$. Then, $\varepsilon = b$ and $\nu = 1 + \varepsilon^{-1} = 8.1$. However, this contradicts the theoretical restriction from above: $\nu \leq 3$. Consequently, it should be $\nu < 1$. In this case, decomposition law (22) is true and can be used to yield:

$$\lambda = 2 + b(1 - \nu). \qquad (25)$$

As $\nu < 1$ and $b > 0$, we have $\lambda > 2$. For the chosen value of b and the theoretical restriction from below $\nu \geq 2/3$, the parameter λ can vary in a very narrow interval: $2 < \lambda < 2.05$, which places stringent restrictions on the asymptotic behavior of the initial distribution of molecules by size.

Consider the reasons that can lead to $\nu < 1$. First of all, it should be noted that the fractal dimension of a surface depends on the scale used to measure this surface. The larger is the scale, the higher is the extent to which the nonuniformity of the surface is leveled off. In this case, its fractal dimension D approaches 2. For enzymatic decomposition, the scale unit is represented by the enzyme molecule, which is rather large as compared to the size of nonuniformities on the surface of the organic macromolecule. Consequently, it should be expected that the fractal dimension of the macromolecule surface measured by this scale will be rather close to 2. At the same time, the fractal dimension d of the volume of an organic molecule will depend on the molecule formation mechanism: $d < 2$ for the cluster–cluster aggregation and $d > 2$ for the particle–cluster aggregation. This implies the following conclusion about the fractal index ν of the molecule: $\nu > 1$ for the cluster–cluster aggregation and $\nu < 1$ or close to 1 for the particle–cluster aggregation. It is also important to take into account the possibility of an internal rearrangement in a macromolecule that may be caused by the re-orientation of the structural units and formation of new ties. During the process of such "ripening", the structure of the macromolecule becomes still more compact, which
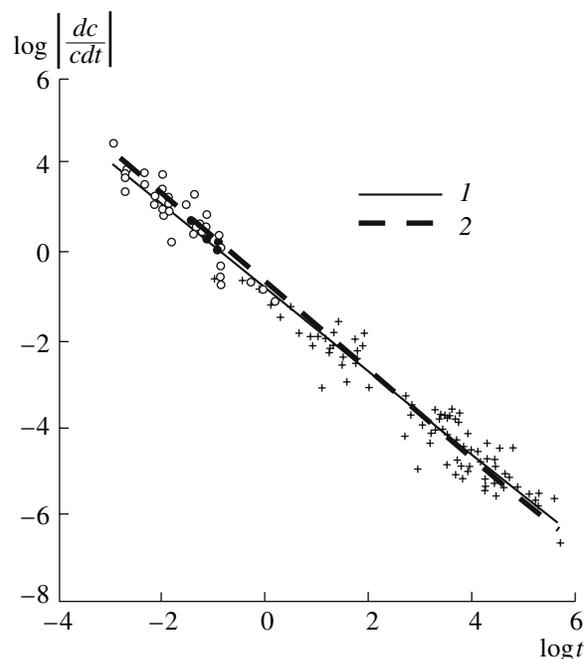

Fig. 2. Decomposition rate of organic matter in sea sediments as a function of time (adopted from the study [35] with some changes). The time on both axes is expressed in years: *1*, quasi-first-order model; *2*, power-law function $c \sim t^{-b}$ with $b = 0.14$.

can affect its fractal dimension d: it will increase, coming closer to the dimension of the physical space, which is equal to 3. It follows from the above that in the system that has been ripening long enough (for example, the organic matter in the bulk water and bottom sediments in the world ocean), the fractal index of organic macromolecules will tend to $\nu = 2/3$.

We will now find out what reason is responsible for the power-law tail in the initial distribution of organic macromolecules by size before the beginning of enzymatic decomposition. Macromolecules in water are synthesized by the coagulation mechanism and the macromolecules themselves play the role of coagulating aggregates. The transformation kinetics of the distribution of aggregates by size is described by the Smoluchowski coagulation equation [36]:

$$\frac{\partial f(n)}{\partial t} = \int_0^{n/2} \beta(n - n', n') f(n - n') f(n') dn'$$
$$- f(n) \int_0^{\infty} \beta(n, n') f(n') dn', \qquad (26)$$

where $\beta(n, n')$ is the frequency of effective (leading to coagulation) collisions of aggregates with dimensions n and n'.

It is shown [37] that for the gradient mechanism of collisions between aggregates with radically different

Parameter	Measured index			
	Color index		COD	
	Water	Water–bot-tom sedi-ment	Water	Water–bot-tom sedi-ment
c_0	500 deg	450 deg	320 mgO/l	334 mgO/l
T, day	62.4	154	99.9	269
ε	0.545	1.34	0.426	2.10
σ, %	2.3	2.9	3.8	4.7

COD, chemical oxygen demand; σ, standard deviation.

dimensions ($n \gg n'$), there is a function $\beta(n, n') \approx \beta_0 n^{3/d}$, where β_0 is the parameter depending on the flow gradient and characteristics of structural units, which provides the rapid increase of the frequency of effective collisions as the aggregates build up. The larger is the aggregate, the higher is the rate at which the aggregate absorbs monomers and small aggregates, decreasing the concentration of these particles in the system. In a finite time, there will be no aggregates with a dimension less than n in the system. This was demonstrated by the numerical experiments with a disperse system in which the coagulation and fragmentation of aggregates proceed [38, 39]. In the case under consideration, there is no fragmentation because the ties between structural units in a macromolecule are rather strong [40] (they are stronger than the tensile stresses in the shear flow of a liquid). As a result, the absorption of aggregates with dimensions less than n will be completed in a far shorter time. After that, new aggregates with dimensions less than n will stop to emerge and the first term in Eq. (26) will reduce to zero. The coagulation will continue due to the collision of aggregates with dimensions starting with n and larger. This gives rise to far larger aggregates and the number of aggregates with dimension n will decrease at a rate determined by the last term in (26). As the forming distribution will slowly decline with increasing dimension, the largest contribution into the integral will be made by aggregates with $n' \gg n$, for which we can use the approximation $\beta(n, n') \approx \beta_0 n'^{3/d}$. Consequently, some time (depending on n) after the coagulation beginning, Eq. (26) takes the form

$$\frac{\partial f(n)}{\partial t} = -\beta_0 f(n) \int_0^\infty n'^{3/d} f(n') dn'. \qquad (27)$$

After the initial stage is coover the coagulation kinetics passes to a self-similar mode [36], in which the size distribution does not have a characteristic scale. This scale could emerge under the action of flow stresses if they are strong enough to detach fragments from the surface of aggregates. In this case, the increase of shear stresses with growing size of aggregates will limit their size by some equilibrium value [37]. However, it does not happen because of the strong ties between the structural units constituting the macromolecule. The absence of a characteristic scale manifests itself as scale invariance, which means that there is a similarity relationship $f(n/s) = s^\lambda f(n)$ for an arbitrary scale s. This immediately results in a power-law distribution $f(n) \sim n^{-\lambda}$. For the integral in (27) to exist, the decline exponent λ should satisfy the condition $3/d - \lambda < -1$, from which we obtain:

$$\lambda > 1 + 3/d. \qquad (28)$$

Since $d \le 3$, $\lambda > 2$, which well agrees with relation (25). If we assume that b and D are known, (25) and (28) can be used to obtain a constraint on the fractal dimension of aggregates:

$$d > \underline{d} \equiv \frac{3 + bD}{1 + b}. \qquad (29)$$

The above analysis shows that the causes of the emergence of the power-law tail of the distribution in the coagulation formation of macromolecules are the rapid growth of the frequency of effective collisions with increasing size of aggregates and the absence of restrictions on the growth of the macromolecules.

Let us use the obtained findings to analyze the data on enzymatic decomposition of lignin [6]. This paper studied the decomposition in bulk water and in a water–bottom-sediment combined system. A part of the experiments was based on the water from the lake Baikal. The lignin concentration was determined by indirect indices, such as the color index and chemical oxygen demand. If the lignin is assumed to be represented by a uniform fraction, the decomposition kinetics will be described by formula (18) (with $\nu > 1$). The results calculated by this formula (Fig. 3) satisfactory agree with the experimental data [33]. The parameters of the kinetic curves found by the method of least squares are summarized in the table:

Parameters of relationship (18) for the curves plotted in Fig. 3

If there is initially a mixture of lignin macromolecules distributed by size by the power law, these data should be processed in a different way. As was shown above, the decomposition kinetics at its asymptotic stage should also follow the power law $c \sim t^{-b}$ [see (22)]. According to the literature data [33], the exponent b, denoted by ε in the paper [33], depends on the process conditions. For example, it is equal to $b = 0.4$ to 0.5 for the decomposition in a bulk water and $b = 1$ to 2 for the decomposition in a water–bottom-sediment combined system. Assuming that $D = 2.2$ in (25) and using the averaged values of b, 0.45 and 1.5, we find that $\underline{d} = 2.75$, $\underline{\lambda} = 2.09$ for the first case and $\underline{d} = 2.52$, $\underline{\lambda} = 2.19$

for the second case, where $\lambda = 1 + 3/\underline{d}$. If according to (29) the fractal dimension is taken a little larger than its lower boundary, specifically $d = 2.80$ and 2.55, we obtain the values of decline exponent $\lambda = 2.1$ and 2.2, respectively.

The conclusion about the power-law distribution by size was referred to the distribution of organic macromolecules $f_0(n)$ formed in water as a result of coagulation. After the enzymatic decomposition begins, the distribution of macromolecules is transformed according to formulas (9) and (10). For $\nu < 1$, we obtain:

$$f(n) \sim n^{-\lambda}\left(1 + \frac{(1-\nu)k_1 t}{n^{1-\nu}}\right)^{-\frac{\lambda-\nu}{1-\nu}}. \tag{30}$$

At a fixed moment of time, distribution (30) for high values of n retains the power-law tail left from the initial distribution:

$$f(n) \sim n^{-\lambda} \quad \text{when} \quad n^{1-\nu} \gg (1-\nu)k_1 t.$$

When a rather long time has been passed since the process beginning, the number of aggregates with given dimension n decreases with time by the power law:

$$f(n) \sim n^{-\nu}[(1-\nu)k_1 t]^{-(\lambda-\nu)/(1-\nu)}$$

$$\text{when} \quad (1-\nu)k_1 t \gg n^{1-\nu}.$$

Consequently, the power-law asymptotic behavior of the distribution of organic molecules is observed for the enzymatic decomposition as well.

CONCLUSIONS

The mechanisms of the enzymatic decomposition of an organic substance consisting of fractal macromolecules of different sizes considered in the present paper made it possible to formulate and solve the kinetic equation of the decomposition and analyze the obtained solutions for two cases, a uniform fraction of macromolecules and a mixture of macromolecules of different sizes.

It was shown that, in the case of a uniform fraction the decomposition can be described by a nonlinear kinetic equation the order of which is equal to the fractal index of the macromolecules (ratio of the fractal dimensions of their surface and volume). The consideration of the reactivity of macromolecules, defined as the rate constant for their decomposition in the kinetic equation of the first order showed that in the decomposition of a uniform fraction the spectrum of the reactivities of macromolecules is given by the gamma-distribution in which the power-law part describes the number of slowly decomposing structures, which are stable with respect to enzymatic decomposition, and the exponential function part accounts for the number of labile (unstable) fractions.

For the decomposition of organic matter represented by a mixture of macromolecules of different sizes, the
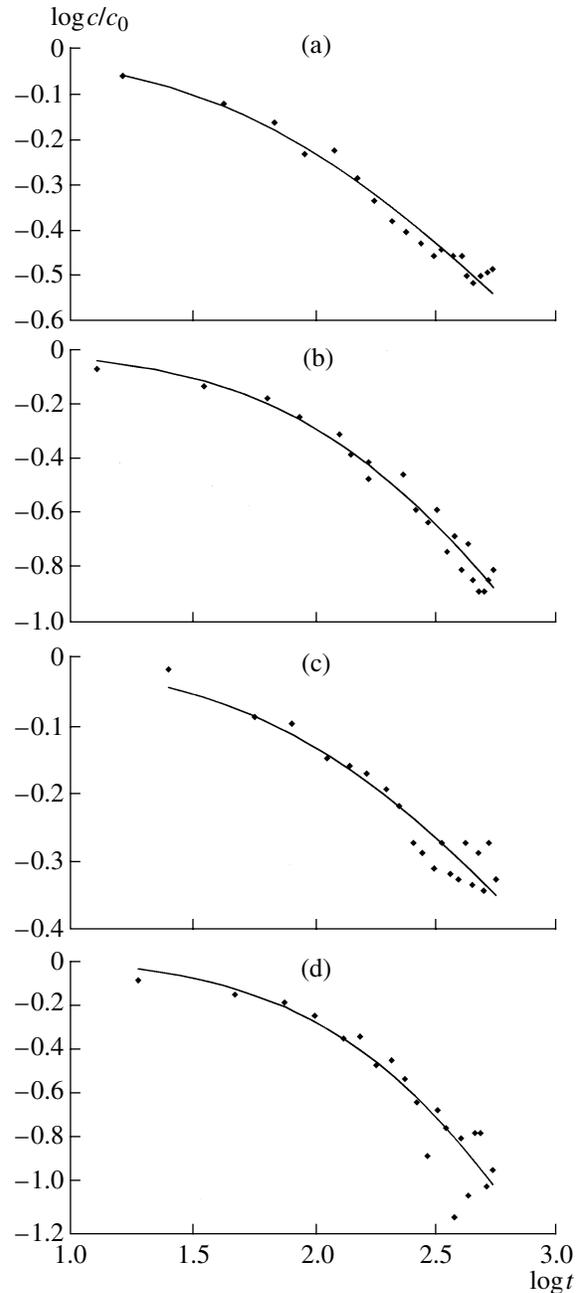

Fig. 3. Decomposition kinetics of lignin determined by (a, b) color index and (c, d) COD in (a, c) homogeneous aqueous medium and (b, d) water–bottom-sediment inhomogeneous system.

decomposition kinetics is determined not only by the fractal structure of the macromolecules but also by the type of their initial distribution by sizes. The latter is formed in water under the action of coagulation mechanisms, which under certain conditions, such as the rapid growth of the frequency of effective collisions with increasing sizes without any restrictions on the growth of macromolecules, accounts for the power-law tail of the distribution with a decline exponent greater than 2.

The distribution developed from the initial power-law distribution due to the decomposition retains the same power-law asymptotic behavior at every moment of time. However, the zone of its action is shifted with time to far larger macromolecules. The number of macromolecules with a given dimension decreases with time by the power law. Under these conditions, the decrease of the concentration of organic matter also follows the power law, in which the exponent depends on the decline exponent in the initial distribution and the fractal index of macromolecules.

Analysis of the literature data on the decomposition kinetics of organic matter in sea bottom sediments and laboratory experiments, which cover a vastly wide time interval from several hours to one million years, showed that the concentration decreases with time by the universal power law with an exponent equal to 0.14. Analysis of the kinetics of enzymatic decomposition of lignin, which is available in the wastewaters discharged by the pulp-and-paper industry, showed that the exponent in this case is equal to 0.4 to 0.5 for the decomposition in a bulk water and 1 to 2 for the decomposition in water with bottom sediments.

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NOTATION

a—exponent in the relationship between the decomposition rate coefficient (constant) and time for the model of quasi-first-order kinetics;

b—exponent in the relationship between the concentration and time for the decomposition of a mixture;

C_1, C_2—additive constants;

c—concentration of organic carbon;

c_0—initial concentration of organic carbon;

D—fractal dimension of the surface of a macromolecule;

d—fractal dimension of the volume of a macromolecule;

$f(n)$—macromolecules size distribution density ;

$f_0(n)$—initial distribution by size.

$g(k)$—spectrum of the reactivities of macromolecules;

k—reactivity of a macromolecule;

k_n—rate constant for the enzymatic decomposition of a macromolecule of dimension n;

N_0—initial concentration of the macromolecules of an organic substance;

N_n—concentration of macromolecules of dimension n;

n—macromolecule dimension defined as the number of carbon atoms in this molecule;

n_0—characteristic dimension of macromolecules before the beginning of decomposition;

R—macromolecule radius;

S—surface area of a macromolecule;

T—characteristic decomposition time of organic matter;

t—time;

V—macromolecule volume;

ε—exponent in the relation between the concentration and time for the decomposition of a uniform fraction;

λ—decline exponent for the tail part of the initial distribution $f_0(n)$;

ν—fractal index of a macromolecule, equal to the ratio of the fractal dimensions of its surface and volume.

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