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## EFFECT OF TEMPERATURE, pH AND SULFATES CONCENTRATION ON KINETIC PARAMETERS OF DESULFURICATION PROCESS

On the basis of the derived kinetic equation, the effect of temperature, pH and initial concentration of sulfates on the rate of desulfurication process, occurring in the presence of *Desulfotomaculum ruminis* bacteria, has been studied. It has been found that the optimal conditions are created at the temperature of 37°C, pH = 7, C/S = 9.

### 1. INTRODUCTION

In one of our previous papers, we have proved that the desulfurication process (dissimilatory reduction of sulfates) occurs according to a kinetic model based on the system of two consecutive, irreversible autocatalytic reactions of the second order [1].

We have also emphasized the role of this process in economy, industry, agriculture, in waste purification and utilization [1]–[9]. Application of this process depends, however, on our knowledge of all factors limiting its rate.

In the kinetic model proposed, the influence of such parameters as temperature, pH and initial concentration of sulfates on the rate of the desulfurication has been examined.

### 2. MATERIALS AND METHODS

Bacteria of *Desulfotomaculum ruminis* were isolated and identified via morphological and physiological studies as well as examination under an electron microscope which was described earlier [5], [8].

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Kinetic studies were performed in tightly closed reactors containing 50 cm<sup>3</sup> of lactate nutrient, whose macro- and micronutrient composition is listed in [1]. The nutrient in reactors was sterilized at the temperature of 120°C for 30 min, then helium was blown through the reactor and 4% of bacterial inoculum after 24 hours of growing were introduced into the nutrient. The reaction was carried out within temperature range from 15 to 44°C, at pH of the environment from 4 to 10, and at the  $C_{org}/S_{SO_4}$  ratio equal to 5, 9, 12 and 18.

Current concentration of sulfates was measured according to a complexometric method involving precipitation of sulfates with the solution of barium chloride and then titration of the excess of barium with the solution of EDTA [10].

Current concentration of sulfites was determined by means of a spectrophotometric method in UV light with a wavelength of 200 nm. In this method absorption of SO<sub>2</sub> released from sulfites after their acidification with a sulfuric acid is measured [11], [12].

Advancement of the reaction was controlled by measuring the current concentration of hydrogen sulfide formed in the course of dissimilatory reduction of sulfates. The hydrogen sulfide produced was absorbed in washers containing 0.02 M solution of cadmium acetate, and the content of sulfides was established iodometrically [10]. Protein concentration was measured according to Lowry's method [13]. Kinetic parameters, statistical analysis of the data and plots were made using an IBM computer with an appropriate software.

### 3. RESULTS AND DISCUSSION

As biological desulfurication is caused by microorganisms sensitive, first of all, to temperature and pH of environment, the examination of the relations between the rate of the desulfurication reaction and these parameters is the main goal.

As it turned out, at extreme temperatures, i.e. 15 and 44°C, the process of dissimilatory reduction of sulfates does not occur. Moreover, the difference in the rate of desulfurication proceeding at 35–38°C is insignificant. Only a decrease or increase of temperature by 10°C does bring about a rapid change in the activity of microorganisms, which is expressed by inhibiting the transformation. The optimum activity is observed at the temperature of 37°C. Kinetic parameters and the coefficients of correlation between experimental and theoretical data calculated for the desulfurication process proceeding at various temperatures (pH = 7, C/S = 9) are compiled in table 1.

In the calculations, the kinetic equations derived previously [1], [8] were used, but the appropriate constant rates ( $k_1$  and  $k_2$ ) and the induction periods of stages of the dissimilatory reduction of sulfates were determined according to a method of nonlinear regression via an appropriate software. As follows from table 1, at the temperature of 37°C the constant rate  $k_1$  and the induction period attain their optimal values, while in the higher and lower temperatures the values of constant

Table 1

Kinetic parameters and correlation coefficients of experimental and theoretical data for reduction process conducted at variable temperatures (pH = 7, C/S = 9)

Temperature (°C)	$k_1$ (l/g × h)	$t_1$ (h)	$k_2$ (l/g × h)	$t_2$ (h)	$r_{SO_4}$	$r_{SO_3}$	$r_s$
20	0.0110	12.4	0.0094	13.5	0.95	0.77	0.99
25	0.0231	6.5	0.0198	10.4	0.98	0.75	0.99
30	0.0372	2.9	0.0328	6.8	0.98	0.86	0.99
37	0.0532	0	0.0392	0.6	0.98	0.89	0.99
39	0.0504	0.2	0.0429	1.0	0.97	0.85	0.99
41	0.0441	1.9	0.0349	2.6	0.93	0.76	0.97

$k_1$  – rate constant of I stage of sulfate reduction.

$k_2$  – rate constant of II stage of sulfate reduction.

$t_1$  – induction time of I stage of reduction process.

$t_2$  – induction time of II stage of reduction process.

$r_{SO_4}$  – correlation coefficient between experimental data and model curve representing sulfate conversion.

$r_{SO_3}$  – correlation coefficient between experimental data and model curve representing sulfite conversion.

$r_s$  – correlation coefficient between experimental data and model curve representing sulfide formation.

rates decrease, and those of induction periods – increase. Only in the case of the constant rate  $k_2$ , its slightly higher value is obtained if the process proceeds at 39°C, but then the induction periods last longer. Results of these studies are illustrated in figures 1 and 2.

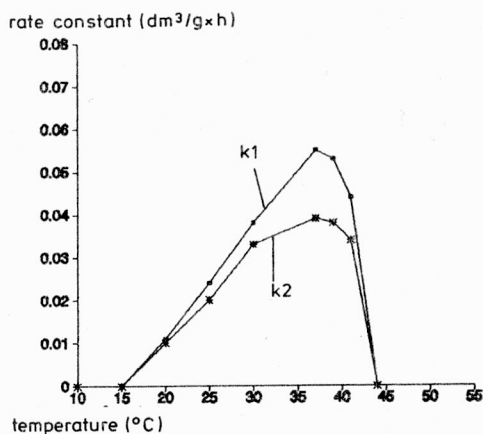


Fig. 1. Temperatures of I and II stages versus rate constants of sulfate reduction

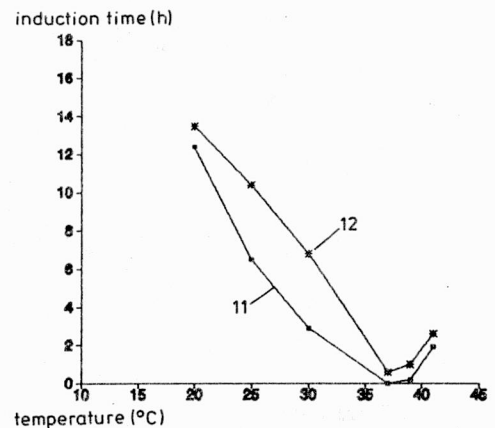


Fig. 2. Temperatures of I and II stages versus induction times of sulfate reduction

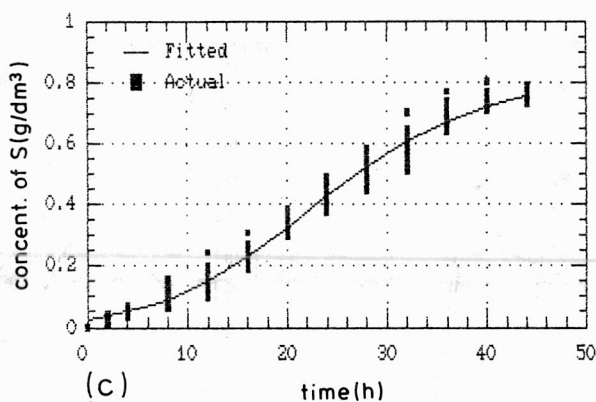
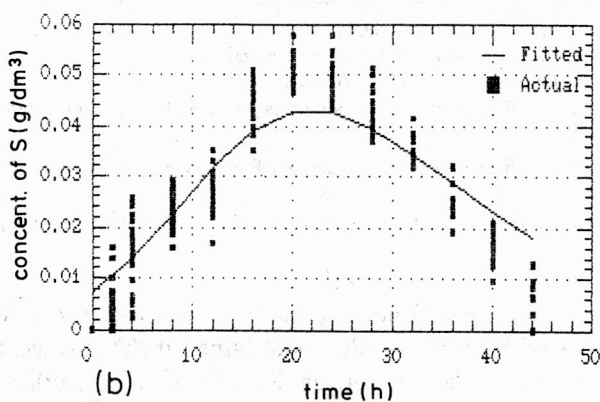
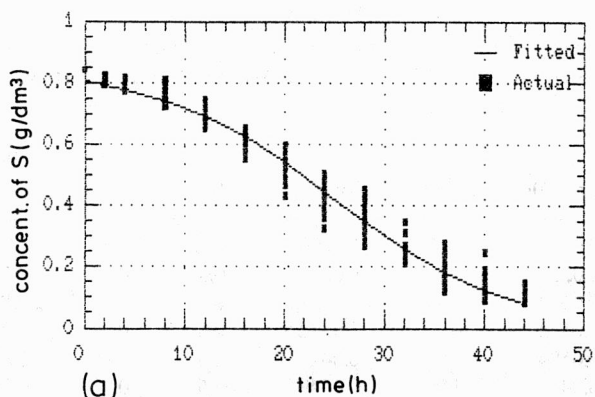


Fig. 3. Correlation between experimental (line) and theoretical (points) data of sulfate reduction,  $r = 0.98$  (a), sulfites reduction,  $r = 0.89$  (b) and sulfides formation,  $r = 0.99$  (c) (temp.  $37^{\circ}\text{C}$ ,  $\text{pH} = 7$ ,  $\text{C/S} = 9$ )

It is interesting to point out here: 1) the correlation between the experimental and theoretical data, and 2) the correlation coefficients determined on the basis of the kinetic model proposed. These data are presented in fig. 3.

Table 2

Kinetic parameters and correlation coefficients of experimental and theoretical data for reduction process conducted under variable pH values (temp. 37°C, C/S = 9)

pH	$k_1$ (l/g × h)	$t_A$ (h)	$k_2$ (l/g × h)	$t_B$ (h)	$r_{SO_4}$	$r_{SO_3}$	$r_s$
5.0	0.0125	6.5	0.0098	7.6	0.99	0.8	0.98
5.5	0.0173	3.6	0.0130	5.5	0.94	0.81	0.85
6.0	0.0282	2.8	0.0232	3.5	0.99	0.81	0.99
6.5	0.0453	1.6	0.0357	2.8	0.97	0.75	0.99
7.0	0.0532	0	0.0393	0.6	0.98	0.89	0.99
7.8	0.0460	2.0	0.0373	2.8	0.89	0.75	0.98
8.5	0.0380	3.4	0.0301	3.9	0.94	0.79	0.97
9.0	0.0323	5.9	0.0253	7.0	0.98	0.76	0.99

$k_1$  – rate constant of I stage of sulfate reduction.

$k_2$  – rate constant of II stage of sulfate reduction.

$t_A$  – induction time of I stage of reduction process.

$t_B$  – induction time of II stage of reduction process.

$r_{SO_4}$  – correlation coefficient between experimental data and model curve representing sulfate conversion.

$r_{SO_3}$  – correlation coefficient between experimental data and model curve representing sulfite conversion.

$r_s$  – correlation coefficient between experimental data and model curve representing sulfide formation.

The investigation of the effect of environment pH on the process rate suggests that desulfurication reaches its optimum at pH = 7. In this case, the most favourable values of the constant rates of reaction and of induction periods are obtained. At pH values higher and lower, the rate constants diminish, while induction periods last longer which means that the total time of the process increases. At the extreme values of pH, i.e. 4 and 10, desulfurication does not take place at all.

Appropriate kinetic parameters calculated according to the model proposed for the reduction occurring at varied pH are listed in table 2 and illustrated in figures 4 and 5. Maximum values of the constant rates of both reaction stages are reached at pH = 7. The same holds for the induction periods at pH = 7. This seems to indicate that the microorganisms controlling this process are more sensitive to acid than to alkaline environment. For example, at pH = 5, the constant rates are 4 times lower than the maximum ones, while at pH = 9, these rates diminish only by 60% with respect to the maximum values. Though this process can proceed within a wide range of pH (from 5 to 9), its rate is reported to be the highest at pH = 7.

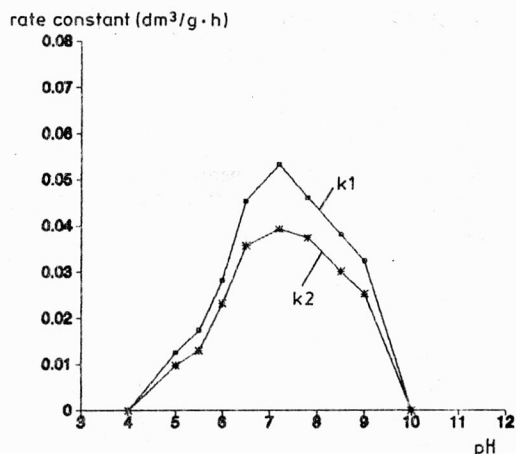


Fig. 4. pH in I and II stages versus rate constants of sulfate reduction

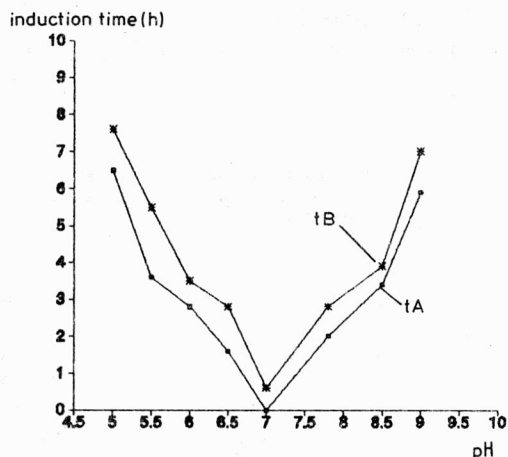


Fig. 5. pH in I and II stages versus induction time of sulfate reduction

Results of laboratory experiments on the effect of initial concentration of sulfates on the course of the desulfurication are presented in table 3 and figure 6.

Table 3

Kinetic parameters and correlation coefficients between experimental and theoretical data for reduction process conducted at variable values of sulfate initial concentration (temp. 37°C, pH = 7)

$[\text{SO}_4^{2-}]_0$	C/S	$k_1$	$t_A$	$k_2$	$t_B$	$r_{\text{SO}_4}$	$r_{\text{SO}_3}$	$r_s$
0.44	18	0.1223	0	0.1018	0.2	0.98	0.76	0.98
0.67	12	0.0712	0	0.0564	0.5	0.99	0.83	0.99
0.84	9	0.0532	0	0.0393	0.6	0.98	0.89	0.99
1.55	5	0.0126	0	0.0088	0.8	0.92	0.70	0.99

$[\text{SO}_4^{2-}]_0$  – sulfate initial concentration.

$k_1$  – rate constant of I stage of sulfate reduction.

$k_2$  – rate constant of II stage of sulfate reduction.

$t_A$  – induction time of I stage of reduction process.

$t_B$  – induction time of II stage of reduction process.

$r_{\text{SO}_4}$  – correlation coefficient between experimental data and model curve representing sulfate conversion.

$r_{\text{SO}_3}$  – correlation coefficient between experimental data and model curve representing sulfite conversion.

$r_s$  – correlation coefficient between experimental data and model curve for sulfides formation.

Constant rates of stages 1 and 2 of sulfate reduction are the highest at the lowest value of the initial concentration of  $\text{SO}_4^{2-}$  and decrease exponentially with increasing initial concentration of sulfates. From the data presented it follows that

the constant rate  $k_1$  calculated for the process occurring at the initial concentration of sulfates equal to  $0.44 \text{ g S}_{\text{SO}_4}/\text{dm}^3$  ( $C/S = 18 \text{ g/g}$ ) is 10 times higher than the corresponding rate constant calculated for the maximum concentration examined (equal to  $1.55 \text{ g S}_{\text{SO}_4}/\text{dm}^3$ ), while the constant rate  $k_2$  is 12 times higher. Differences in the values of constants at extreme sulfate initial concentrations are markedly greater than the corresponding differences in the values of extreme temperatures or extreme pH. It should be also mentioned that the values of induction periods for second stage are insignificant with respect to the duration of the process. For the

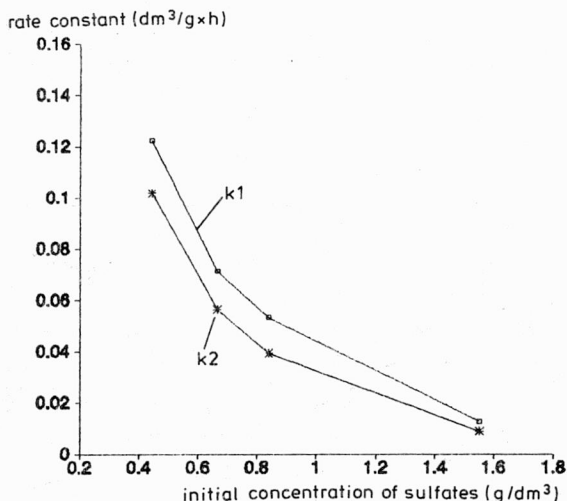


Fig. 6. Sulfate initial concentration in I and II stages versus rate constants of sulfate reduction

whole process, the optimal value of the initial concentration of sulfates was considered to be  $0.84 \text{ g/dm}^3$ , or in other words, the  $C/S$  ratio was 9. At the values of the initial concentration greater than  $1.55 \text{ g S}_{\text{SO}_4}/\text{dm}^3$ , desulfurication does not take place at all.

The dependence of constant rates for both stages of the desulfurication on temperature, pH and initial concentration of sulfates was approximated by analytical functions. This enabled us to calculate quickly kinetic parameters of the reduction process taking place under optimal conditions, i.e., at:

pH = 7,  $T = 37^\circ\text{C}$ , variable  $[\text{SO}_4^{2-}]_0$ ,

pH = 7,  $[\text{SO}_4^{2-}]_0 = 0.84$ , variable  $T$ ,

$T = 37^\circ\text{C}$ ,  $[\text{SO}_4^{2-}]_0 = 0.84$ , variable pH.

Dependence of constant rates on pH was approximated by square function. In the case of the dependence of  $k_1$  on pH, it takes the following form:

$$k_1 = ax^2 + bx + c \quad (1)$$

where:  $x$  - pH value,  $a = -0.005$ ,  $b = 0.074$ ,  $c = -0.224$ .

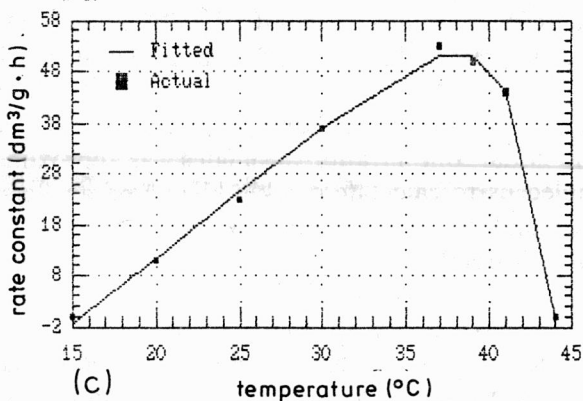
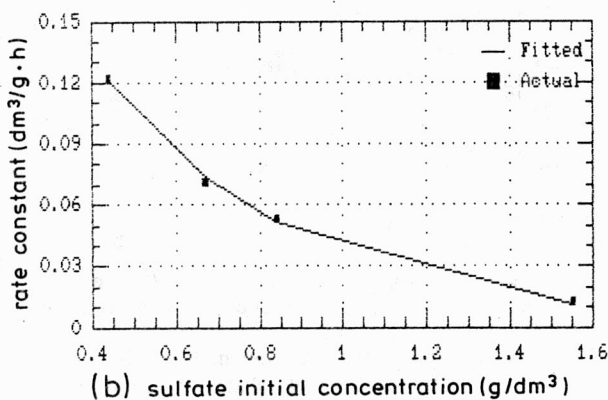
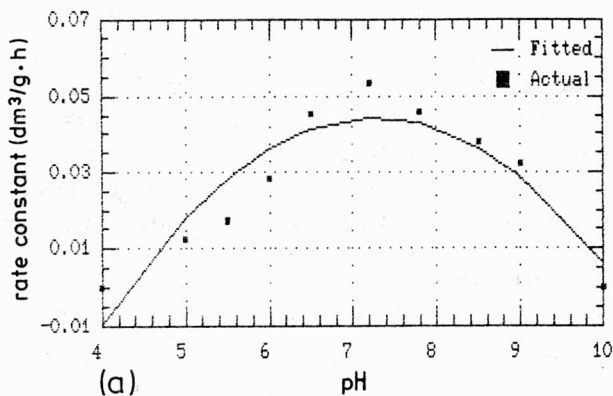


Fig. 7. Functions describing the dependence of rate constant on pH,  $r = 0.9$  (a), sulfate initial concentration,  $r = 1$  (b) and temperature,  $r = 1$  (c) (temp.  $37^\circ\text{C}$ , pH = 7, C/S = 9)



For the dependence of  $k_2$  on pH, the function has the same form, only the values of  $a$ ,  $b$  and  $c$  parameters change as follows:  $a = -0.004$ ,  $b = 0.058$ ,  $c = -0.176$ .

The correlation coefficient between the function proposed and experimental data is equal to 0.9, and a respective dependence of constant rates on pH values is illustrated in figure 7a.

Dependence of constant rates on the initial concentration of sulfates was approximated with exponential function, which for both constant rates takes the form:

$$k = e^{a+bx}, \quad (2)$$

the values of  $a$  and  $b$  for the constant rate  $k_1$  are as follows:  $a = -1.169$ ,  $b = -2.138$ ; and for the constant rate  $k_2$  they are:  $a = -1.233$  and  $b = -2.405$ .

The correlation coefficient between the exponential function proposed and the experimental data is 0.998, and the dependence of constant rates of initial concentration of sulfates is shown in figure 7b.

As far as the dependence of constant rates on temperature is concerned, the former tend to increase linearly with temperature, until they reach the maximum at 37°C, and afterwards their values rapidly drop.

Therefore, this dependence was approximated with a function which is a difference of the linear and exponential functions:

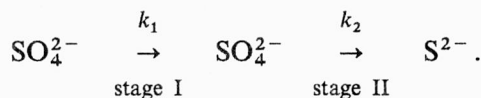
$$k = at + b - e^{c(t-d)} \quad (3)$$

where  $t$  is temperature; for  $k_1$ :  $a = 0.0026$ ,  $b = -0.04$ ,  $c = 0.412$ ,  $d = 50.35$ , for  $k_2$ :  $a = 0.0021$ ,  $b = -0.032$ ,  $c = 0.386$ ,  $d = 51.28$ .

In this case, the correlation coefficient assumes the values of 0.997, and the corresponding curve is shown in figure 7c.

Great values of correlation coefficients testify to a strong relationship between the experimental data obtained and the model proposed within the whole range of the studied temperature, pH and initial concentration of sulfates.

Therefore, on the basis of the first and the second part of this paper we have come to a conclusion that the process of dissimilatory reduction of sulfates may be well described by two irreversible, autocatalytic consecutive reactions of the second order, according to the following diagram:



The equations derived permit an exact determination of kinetic parameters of the process and of the factors significantly affecting its course. Thus, they are of high cognitive value. Besides, these equations can be used to control the course of dissimilatory reduction of sulfates. They can also be suitable for designing systems with an optimal rate of the process under industrial conditions, which concerns primarily such processes as waste purification and utilization and soil recultivation.

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WPLYW TEMPERATURY, pH I STĘŻENIA SIARCZANÓW  
NA PARAMETRY KINETYCZNE DESULFURYKACJI

Na podstawie wyprowadzonych równań kinetycznych przebadano wpływ temperatury, pH i początkowego stężenia siarczanów na szybkość procesu desulfurykacji, który zachodzi z udziałem bakterii *Desulfotomaculum ruminis*. Stwierdzono, że warunki optymalne tego procesu przypadają na temperaturę 37°C, pH = 7 i C/S = 9.

ВЛИЯНИЕ ТЕМПЕРАТУРЫ, pH И КОНЦЕНТРАЦИИ СУЛЬФАТОВ  
НА КИНЕТИЧЕСКИЕ ПАРАМЕТРЫ ОБЕССЕРЕНИЯ

На основе выведенных кинетических уравнений исследовано влияние температуры, pH и начальной концентрации сульфатов на скорость процесса обессерения, который протекает с присутствием бактерий *Desulfotomaculum ruminis*. Было установлено, что оптимальные условия этого процесса это: температура 37°C, pH=7 и C/S=9.