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WET OXIDATION OF DAIRY SEWAGE

MOKRE UTLENIANIE ŚCIEKÓW PRZEMYSŁU MLECZARSKIEGO

Abstract: Results of kinetic studies on the process of wet oxidation of dairy sewage are presented. Experiments were carried out in a stirred batch tank reactor at the oxygen partial pressure equal to 1 MPa and at temperature ranging from 473 to 523 K. Dairy sewage was subjected to oxidation at a natural pH close to 4. The efficiency of decomposition of organic compounds was estimated on the basis of TOC measurement. The highest TOC reduction rate reached 79.6%. A kinetic model of the process was proposed and its parameters were determined experimentally. Good agreement of the experimental and calculated results was obtained.

Keywords: wet oxidation, dairy sewage, kinetic model

One of the most significant environmental problems in dairy industry is the release of process sewage to surface water. Dairy products are manufactured in milk collecting and dairy plants which generate process sewage characteristic of individual process lines. Majority of dairy sewage consists of diluted solutions mainly of emulsified fat, colloidal protein and sugar, ie lactose. Additionally, it may contain various minerals (eg calcium salts and phosphates) and vitamins, enzymes and other organic compounds [1].

The discharge of dairy sewage to surface water may lead to very unfavorable phenomena such as high oxygen demand, sewage sludge deposition, sewage fungus growth and decreased pH of receiving water. From the biochemical point of view, dairy sewage is relatively burdensome because of putrefaction caused by the presence of lactose which is decomposed to lactic acid, butyric acid and carbon dioxide. This, in turn, causes that pH value decreases to below 2. Consequently, such low pH leads to the interruption of acid fermentation and to the precipitation of proteins. A high content of organic acids causes that the BOD₅ to COD ratio varies considerably from domestic sewage and is on the average level of 0.69. This is the reason why researchers look for efficient methods of dairy sewage treatment and removal of lactose being the major environmental threat. Wet oxidation is one of the options of dairy sewage treatment which causes degradation of organic pollutants contained in the sewage.

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Wet oxidation is a method to decompose organic and inorganic components dissolved or suspended in the aqueous phase. This process is based on the oxidation at high temperature ranging from 398 to 573 K and under high pressure of 0.5÷20 MPa. To oxidize pollutants, either oxygen or air is pumped into the reaction medium. Pressure and temperature used in wet oxidation significantly improve the method efficiency thanks to better solubility of oxygen at high temperatures and increased reaction rates. This process is carried out in the aqueous phase due to the application of elevated pressure that is higher than water vapor pressure above the solution. For this reason, the liquid does not come to boiling at high temperatures. The wet oxidation process is highly non-selective. Most frequently, organic compounds are not decomposed completely, but as a result of the proceeding processes they are converted into intermediate products which are usually less toxic and require less oxygen for their further degradation [2, 3].

Kinetic studies of the wet oxidation process cover mainly wet oxidation of sewage sludge from municipal wastewater treatment plants [4-7] and harmful and toxic organic compounds [8, 9]. For this type of processes several kinetic models were proposed and their quality was evaluated experimentally [10]. In the literature, there are no references to the wet oxidation of pollutants contained in the dairy sewage. Results of researches on a similar subject were presented by Chia et al [11]. Experiments were conducted using lactose solution at 423÷443 K, pressure about 0.7 MPa, in the presence of Pt/Al₂O₃, CeMn and Pt/CeMn catalysts, in order to find an alternative method for the treatment of sewage from cheese production. Much more attention was paid to the catalytic decomposition of lactose to an intermediate product - lactobionic acid which is a commercial product [12-14]. In the case of dairy sewage, this solution is not feasible due to the presence of other substances in the sewage.

In this investigation, the kinetic studies of wet oxidation process of dairy sewage were carried out. A simple kinetic model of the process was proposed and its all characteristic parameters were determined.

Experimental

The experimental material was taken from a traditional dairy plant which processes 80 000 dm³ of milk a day on average.

Table 1

The average parameters of sewage subjected to wet oxidation

	Value
pH	7.32
BOD ₅ [mg O ₂ /dm ³]	1000
COD [mg O ₂ /dm ³]	2215
Total phosphorus [mg P/dm ³]	6.73
Sulphates [mg/dm ³]	54.60
Chlorides [mg/dm ³]	112.80
Ether extract [mg/dm ³]	156.83
Total suspended solids [mg/dm ³]	339.50
Ammonium nitrogen [mg/dm ³]	2.84
TOC [mg/dm ³]	167.9÷289.8

The dairy plant specializes in the production of 2 and 3.2% fresh milk, cream, cottage cheese, natural and fruit yogurt, yogurt drinks, cheese, kefir, buttermilk and butter. Most of these products are manufactured in the plant using traditional production methods. Sewage samples taken for the experiments came from a collective well in which sewage from all manufacturing processes and from washing of machines and equipment were collected. Average parameters of the sewage subjected to analysis are given in Table 1.

The process of wet oxidation of sewage was conducted in a 0.6 dm³ laboratory tank reactor. Figure 1 shows a diagram of the apparatus.

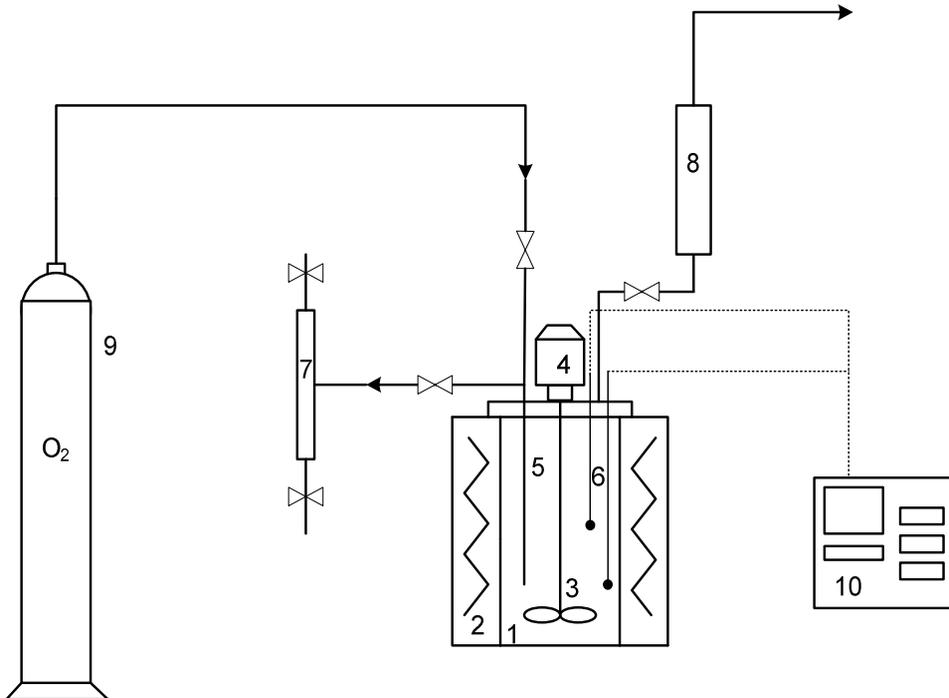


Fig. 1. Diagram of the experimental reactor: 1 - reactor, 2 - heating jacket, 3 - stirrer, 4 - motor of the stirrer, 5 - gas inlet/sample collecting, 6 - temperature and pressure meters, 7 - water-cooled sampler, 8 - cooler, 9 - oxygen cylinder, 10 - control and measuring system

Each time 0.4 dm³ of tested solution (dairy sewage) was introduced to the reactor. After reaching the desired temperature, oxygen was supplied to the reactor, thereby generating assumed overpressure. The sum of partial pressure of water vapor and oxygen was maintained on a constant level. Samples of the reaction mixture were taken in the process to determine *total organic carbon* (TOC). The samples were taken prior to the process and then after 300, 600, 1200, 1800, 2700, 3600 seconds. After taking each sample, the amount of flowing oxygen was corrected so as to keep pressure in the reactor on the same level as before sampling. In these experiments the process of wet oxidation was carried out for different operating conditions (Table 2).

Table 2

Operating conditions of wet oxidation of dairy sewage

No.	Temperature	Partial pressure of oxygen	C _{A0} (TOC)	pH ₀
	[K]	[MPa]	[mol C/m ³]	-
1	453	1	150.89	3.98
2	473	1	184.94	3.98
3	493	1	204.00	4.36
4	503	1	194.07	4.05
5	523	1	209.49	4.79

The coulometric method was used to determine total organic carbon content in the tested reaction mass. Behr C30IRF apparatus was used in the experiments. Prior to the measurements, a boat was pre-fired until reaching a constant value of blank test. When three repeatable values were obtained, their average was introduced to the computer system and the sample analysis could start. A sample of specified volume, which in this case was 0.5 cm³ was supplied to the boat with the use of a pipette. Earlier, the samples were acidified with hydrochloric acid to remove inorganic carbon. Next, the boat with the sample was introduced into the glass combustion tube where oxygen was supplied at the volume flow rate of 60 dm³/h. The sample was burned in the IR furnace at 473 K for the first 2 minutes and then at 1223 K for another 5 minutes. As a result of the sample combustion, organic carbon contained in the sample was converted to the final products of combustion - CO₂ and H₂O. Then, carbon dioxide was completely absorbed in an absorption column filled with barium perchlorate solution. A constant pH level equal to 10 was kept in the column during the analysis, and each change was recorded and transmitted in the form of carbon content in the sample. The measurement for each sample was performed several times to confirm correctness of the result.

Results

The experiments allowed us to determine the effect of process temperature on the degree of decomposition of organic compounds contained in dairy sewage to CO₂ and H₂O. Table 3 gives results of the analysis of samples taken during the wet oxidation process.

Table 3

Changes in relative concentrations of organic carbon in the samples taken during wet oxidation of dairy sewage (TOC_t/TOC₀)

No.	0 s	300 s	600 s	1200 s	1800 s	2700 s	3600 s
1	1.000	0.907	0.829	0.828	0.820	0.811	0.768
2	1.000	0.821	0.756	0.707	0.594	0.581	0.555
3	1.000	0.753	0.648	0.494	0.392	0.370	0.366
4	1.000	0.708	0.597	0.445	0.365	0.282	0.273
5	1.000	0.659	0.436	0.305	0.240	0.212	0.204

The wet oxidation process conducted at low temperature (453 K) caused a small degree of organic material decomposition, not exceeding 25% compared with the initial value of TOC. Elevation of the process temperature caused an increase of process rate and conversion degree of organic compounds to carbon dioxide and water. The degree of

decomposition reached maximum 79.6% at 523 K. The examinations showed that temperature had a decisive influence on the efficiency of removal of organic compounds from the sewage mixture. During the process of wet oxidation of dairy sewage, pH of the mixture changed. Figure 2 shows changes of pH in the tested samples.

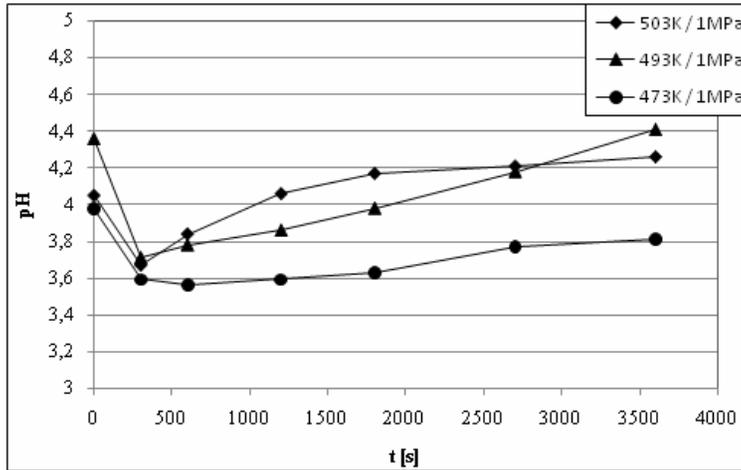


Fig. 2. Change of pH of the reaction solution during wet oxidation process

The pH of the sewage samples significantly decreased mostly during the first 300 seconds of the process, which was a result of the conversion of organic compounds to carboxylic acids. The increase of pH might be a result of decomposition of previously formed acids. Changes in the pH show that the process consists of several stages. An increase in the pH over the initial value for raw sewage was reported for higher temperatures of the experiment. This is a very positive phenomenon, not only because the sewage with low pH has a negative impact on receivers, but also taking into account the transmission possibility and the impact of sewage on the main network.

Kinetic model

Based on the experimental results it was found that organic compounds contained in the sewage were converted to CO_2 and H_2O or final products containing TOC. On this basis, the following scheme of reaction was proposed (Fig. 3):

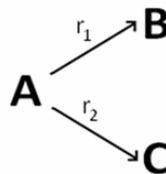


Fig. 3. The proposed scheme of dairy sewage oxidation: A - dairy sewage, B - organic intermediate products that contain TOC, not undergoing further decomposition in the applied range of temperature, C - inorganic products (CO_2 and H_2O)

The above scheme of dairy sewage oxidation and the obtained experimental data were used in a mathematical description of the process in a batch tank reactor with perfect stirring. It was assumed that both reactions were of the first order (Fig. 3). Hence, their rates are described by the following equations:

$$r_1 = k_1 \cdot C_A \quad (1)$$

$$r_2 = k_2 \cdot C_A \quad (2)$$

where:

$$k_i = k_{i0} \cdot \exp\left[-\frac{E}{RT}\right] \text{ and } i = 1 \dots 2 \quad (3)$$

The mass balance for each reactant of the liquid phase has the form:

$$\frac{dC_A}{dt} = r_1 + r_2 \quad (4)$$

$$\frac{dC_B}{dt} = r_1 \quad (5)$$

$$\frac{dC_C}{dt} = r_2 \quad (6)$$

Owing to the form of relations (1)-(2), equations (4)-(6) are the linear differential equations which can be solved analytically. The analytical solutions have the following form:

$$C_A = C_{A0} \cdot e^{-(k_1+k_2)t} \quad (7)$$

$$C_B = C_{A0} \cdot \frac{k_1}{k_1 + k_2} \cdot [1 - e^{-(k_1+k_2)t}] \quad (8)$$

$$C_C = C_{A0} - C_A - C_B \quad (9)$$

Due to the fact that the content of organic carbon determined in the samples is the sum of concentrations of initial substance A decreasing during the experiment, and the increasing concentrations of substance B, the conversion of TOC takes the form:

$$\alpha = \frac{1}{k_1 + k_2} \cdot [k_1 + k_2 e^{-(k_1+k_2)t}] \quad (10)$$

where:

$$\alpha = \frac{C_A + C_B}{C_A} = \frac{\text{TOC}_i}{\text{TOC}_0} \quad (11)$$

The obtained experimental data and the proposed kinetic model of the process (equation (10)) are used to identify all kinetic parameters of this model. The parameters are determined by minimizing the quality index defined by the formula:

$$I(\mathbf{p}) = \sum_{j=1}^n \sum_{i=1}^m (\alpha_{ij}^{\text{exp}} - \alpha_{ij})^2 \quad (12)$$

where \mathbf{p} is the vector of kinetic parameters for reaction (1) and (2)

$$\mathbf{p} = [k_{01}, E_{A1}, k_{02}, E_{A2}]^T \quad (13)$$

In the assumed quality index, internal summation refers to the time of sampling, while external one to the process temperature. A minimum quality index was determined by the Marquardt method [15]. Table 4 gives the values of kinetic parameters that minimize the quality index.

Kinetic parameters of the model reaction

Table 4

	Unit	Value
k_{01}	$[s^{-1}]$	0.0422
E_1	$[J/mol]$	$1.88 \cdot 10^4$
k_{02}	$[s^{-1}]$	$1.2418 \cdot 10^4$
E_2	$[J/mol]$	$6.81418 \cdot 10^4$

A comparison of experimental results and results calculated using the proposed kinetic model is illustrated in Figure 4 and Table 5. The obtained results show good agreement of both types of results.

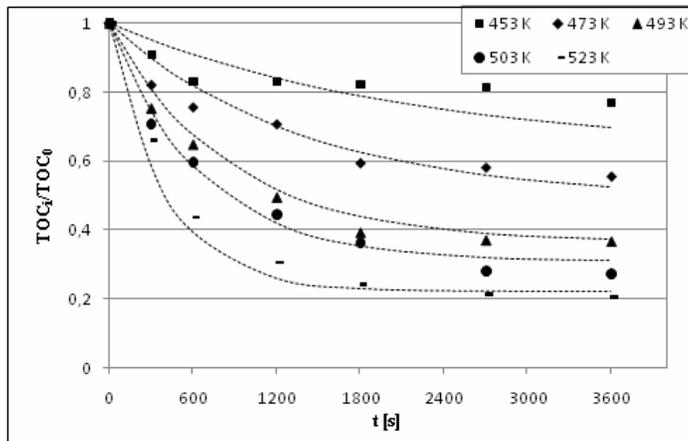


Fig. 4. Changes of relative TOC concentrations in wet oxidation of dairy sewage at various temperatures ($P_{O_2} = 1$ MPa)

Reaction rate constants for individual processes of wet oxidation of dairy sewage ($P_{O_2} = 1$ MPa)

Table 5

No.	T	k_1	k_2	Correlation coefficient*
	[K]	$[1 \cdot s^{-1} \cdot 10^{-4}]$		
1	453	2.8715	1.7342	0.880
2	473	3.5458	3.725	0.976
3	493	4.3041	7.5201	0.996
4	503	4.7148	10.463	0.995
5	523	5.5986	19.504	0.994

*Determines the relation between the experimental and calculated values

Figure 5 shows dependence of rate constants of reaction (1) and (2) on the process temperature.

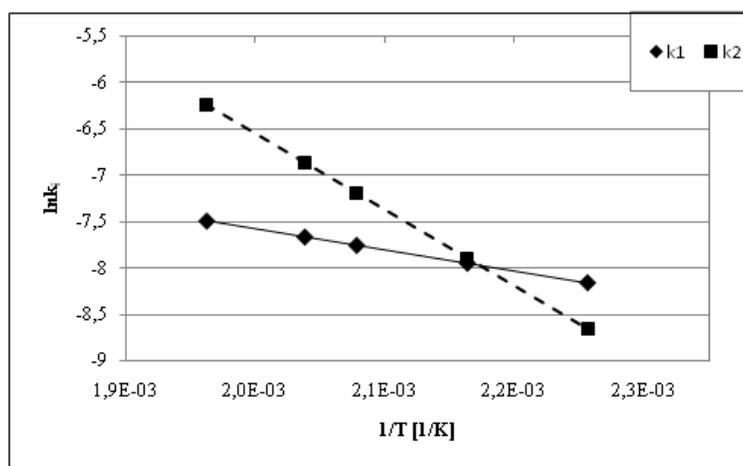


Fig. 5. Dependence of the reaction rate constants on process temperature

In the case of wet oxidation process of dairy sewage conducted at high temperatures (493–523 K), the value of k_2 exceeds significantly the value of k_1 . The reaction rate constant k_2 reflects the rate of conversion of organic carbon to carbon dioxide and water. So, the process conducted at high temperatures is oriented mainly to the decomposition of organic compounds, which results in a high TOC reduction (Table 3). However, wet oxidation carried out at low temperatures (453–473 K) is characterized by the k_2 to k_1 ratio less than unity. Hence, the process carried out in this temperature range leads to the conversion of organic compounds into non-degradable substances. The result is a relatively small degree of TOC reduction (Table 3).

Conclusions

The experimental results show that organic compounds contained in dairy sewage are resistant to the decomposition to carbon dioxide and water. However, they are converted to other organic substances. The highest degree of TOC reduction of sewage was 79.6% at 523 K, under the partial pressure O_2 equal to 1 MPa. Rising process temperature caused an increase in TOC reduction, so that further increase could result in an overall reduction of organic compounds in the sewage. A kinetic model of wet oxidation process was proposed and its kinetic parameters were determined based on experimental data. The results of the proposed model show good agreement with experimental data.

Nomenclature

- A, B, C - reagents
- C - molar concentration [mol m^{-3}]
- E - activation energy [J mol^{-1}]

k	- reaction rate constant [s^{-1}]
P_{O_2}	- partial pressure of oxygen [MPa]
\mathbf{p}	- vector of kinetic parameters
r	- reaction rate [$mol\ m^{-3}\ s^{-1}$]
R	- universal gas constant [$J\ mol^{-1}\ K^{-1}$]
t	- time [s]
T	- temperature [K]
TOC	- total organic carbon [$mol\ C\ m^{-3}$], [$mg\ dm^{-3}$]
α	- degree of sewage conversion

Indexes

0	- initial conditions
A, B, C	- refers to reagents
exp.	- experimental value
m	- refers to measurement time
n	- refers to process temperature

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MOKRE UTLENIANIE ŚCIEKÓW PRZEMYSŁU MLECZARSKIEGO

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Abstrakt: W pracy przedstawiono wyniki badań kinetycznych procesu mokrego utleniania ścieków przemysłu mleczarskiego. Badania przeprowadzono w okresowym reaktorze zbiornikowym z mieszadłem, przy ciśnieniu cząstkowym tlenu $P_{O_2} = 1$ MPa, w zakresie temperatury od 473 do 523 K. Utlenianiu poddawano ścieki mleczarskie o ich naturalnym odczynie zbliżonym do wartości 4. Oceny efektywności rozkładu związków organicznych dokonano na podstawie pomiaru wartości TOC. Najwyższy stopień redukcji TOC ukształtował się na poziomie 79,6%. Zaproponowano model kinetyczny procesu i na podstawie badań eksperymentalnych określono jego parametry. Uzyskano dobrą zgodność wyników doświadczalnych i obliczeniowych.

Słowa kluczowe: mokre utlenianie, ścieki mleczarskie, model kinetyczny