# Influence of The Waste Oil Concentration in Water on The Efficiency of The Aeration Process in Refinery Wastewater Treatment

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Process, aeration system and aeration method for biological treatment of wastewater with activated sludge in bio-aeration tanks are chosen based on the flow parameters, composition of the wastewater and required characteristics of the purified water. Choosing an aeration system is a very complex question, as the capacity of oxygen introduced into the wastewater should correspond to the oxygen consumption in order to achieve the most efficient purification.

This paper presents the results of experimental aeration analysis of water contaminated with waste motor oil with variations of airflow introduced into the water. The processes of clean water aeration and water with different oil content (mass concentration from 5 to 10 mg/L). The purpose of these investigations performed on an experimental setup were analysis of the aeration process technical indicators in correlation with the thermodynamic and kinetic parameters, related to the presence of oil in the water in order to achieve more efficient refinery wastewater purification.

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## 0 INTRODUCTION

Almost all production lines and auxiliary installations in refineries create certain amounts of wastewater containing oil during the production process. Refinery wastewater contains large amounts of oil that is removed in tanks using scrapers during pre-treatment processes. Floculation-sedimentation and floculation-flotation processes are used for complete removal of free hydrocarbons from water. After that, the water is biologically purified in tanks with activated sludge or in aerated lakes and lagoons.

Efficiency of aerobic biological processes in wastewater depends on the amount of dissolved oxygen introduced by aeration system. When aeration systems are designed, it is necessary to use aeration devices with an actual oxygen introduction capacity higher or equal to the actual need for oxygen in a certain phase of the treatment process of wastewater. Introduction of the necessary amount of air into bio-aeration tank and mixing of the whole

suspension in the tank requires knowledge of technical characteristics of the aeration device (coefficient of oxygen transport, oxygen introduction capacity, oxygen transport efficiency and energy efficiency of oxygen transport). The coefficient of oxygen transport,  $k_L a$  is the basic parameter for defining efficiency of the refinery wastewater aeration process.

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Some of the technical indicators of aeration process installations stated in the literature and in the technical documentation of the producers for conditions of clean water aeration are supplied. Technical characteristics of an aeration process in the wastewater were determined in an experimental installation for clean water and water with 5 and 10 mg/L motor oil concentration and presented in this paper. Also the correlation of oxygen transport coefficient with thermodynamic and kinetic parameters related to the presence of oil in the water and air flow velocity were examined in order to achieve more efficient refinery wastewater purification.

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# 1 EXPERIMENTAL INSTALLATION AND DESCRIPTION OF THE INVESTIGATED PROCESS

The actual coefficient of oxygen transport was determined in an experimental installation by enriching water with oxygen. Dissolved oxygen was first chemically extracted from water and then waste oil with a defined mass concentration, was introduced in the water.

A polypropylene column with dimensions 700x700x2200 mm with accompanying connections and construction frame, was used for experimental work in batch conditions. The cross-section surface of the column was determined according to recommendations for an air distributor.

Experimental work was performed for batch working conditions and varying air flow of 2 and 10 m<sup>3</sup>/h. The water level in the column was 2m high and total volume was 980 liters. Water aeration with waste oil content of 5 and 10 mg/L was performed. Dissolved oxygen was previously removed using a chemical method of introducing

sodium-sulfate in the presence of a cobaltchloride hex-hydrate catalyst. Investigation of clean water aeration not containing dissolved oxygen was also performed, in order to compare process parameters for air distribution in standard research conditions with the ones obtained in actual conditions for wastewater with corresponding characteristics.

Fig. 1 shows the experimental installation for investigating the influence of oil in water on the efficiency of the aeration process for different air flow values [1]. Table 1 contains a list of measured values and instruments on the described installation.

The column was initially filled with previously prepared water from which oxygen was extracted using a chemical method. After that, a determined amount of waste oil was added into the water.

Before experiment started, kinematical viscosity, density and surface tension of water in the experimental installation, had to be determined.

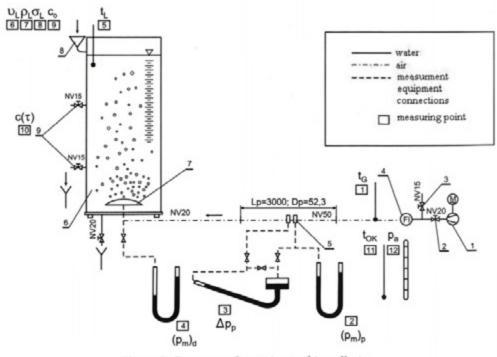


Figure 1. Diagram of experimental installation

1 – low pressure compressor; 2 –air inflow pipe valve; 3 – relief valve; 4 – air flow regulator; 5 – air flow measuring orifice plate; 6 – column with corresponding connections and framework; 7 – disk-shaped membrane air distributor; 8 – water supply; 9 – sampling connection

Complete experimental system defining process parameters of water aeration with certain characteristics, started by measuring the temperature of the surrounding air and water in the column. The over-pressure value before the distributor  $(p_m)_d$  and the orifice plate  $(p_m)_p$  i.e. the pressure difference before and after the orifice plate  $(\Delta p_n)$ , was measured, when the first air bubbles entered in the water. Air flow regulation was performed using a flow regulator and relief valve until a set value for the applied analysis system was attained. When the flow is stabilized, water samples were taken from the column in equal time intervals starts ( $\Delta \tau = 60$  s) and the dissolved oxygen content was measured until the same value appeared three times. After one regime was analyzed, the compressor was switched off and the relief valve was opened completely. Water from the column was released into drains via a draining valve. The column was then filled with a fresh amount of water. Thus, the installation was ready for a new investigation regime, i.e. the described procedure was repeated.

# 2 DETERMINING TECHNICAL INDICATORS OF THE AERATION PROCESS

Oxygen transport coefficient  $k_L a$  is a parameter used to determine the transport intensity of oxygen in water, i.e. the value at which the equilibrium state is reached.

Oxygen transport coefficient is calculated as the product of the oxygen transport coefficient in water  $k_L$  and the specific surface of the contact between air and water in the aeration process (a).

Based on the material balance of oxygen flow through the batch reactor with complete mixing the general equation of material balance is:

$$Qc_{in} + V_G c_{ul} - V_L R(\tau) = Qc + V_G c_{iz} + V_L \frac{dc}{d\tau},$$
 (1)

where:

 $V_G$  - air flow, m<sup>3</sup>/s,

Q - water flow (for batch process conditions Q = 0), m<sup>3</sup>/s,

Table 1. Description of measuring equipment (list of measured values and instruments)

(	Measured value	Denotation	Unit	Instrument		
1.	Air temperature	t <sub>G</sub>	°C	Mercury thermometer		
2.	Air over-pressure	(p <sub>m</sub> ) <sub>p</sub>	mm Hg	U-pipe with mercury		
3.	Pressure loss through the orifice plate	$\Delta p_{\rm p}$	mm Alc	Micro manometer with alcohol		
4.	Air over-pressure in front of the air distributor	$(p_{\rm m})_{\rm d}$	mm Hg	U-pipe with mercury		
5.	Water temperature in the column	t <sub>L</sub>	°C	Mercury thermometer		
6.	Kinematical viscosity of water in the column	U <sub>L</sub>	m <sup>2</sup> /s	Modified Oswald viscosimeter		
7.	Water density in the column	PL	kg/m³	Laboratory pycnometer		
8.	Water surface tension	$\sigma_{\!\scriptscriptstyle L}$	N/m	Microbalance		
9.	Starting mass concentration of dissolved oxygen in water	C <sub>o</sub>	mg/L	"HANNA INSTRUMENTS 9142"		
10.	Mass concentration of dissolved oxygen in water	C(T)	mg/L			

c<sub>in</sub> - mass concentration of oxygen in the influent, kg/m<sup>3</sup>,

 c - mass concentration of oxygen in the effluent, kg/m³,

c<sub>ul</sub> - mass concentration of oxygen in air at the input, kg/m<sup>3</sup>,

c<sub>iz</sub> - mass concentration of oxygen in air at the output, kg/m<sup>3</sup>,

 $R(\tau)$  - specific oxygen consumption during biological treatment, kg/(m<sup>3</sup>·s),

 $V_{\rm L}$  - water volume, m<sup>3</sup>.

The gas phase material balance gives:

$$\dot{V}_G(c_{ul}-c_{iz})=AK_L[c^*(c_{iz})-c],$$
 (2)

where:

 $c^* = c^*(c_{iz})$  - equilibrium mass concentration of oxygen in dependence on the mass concentration of oxygen in air at the output, kg/m³,

 $A = aV_L$ - total contact surface between air and water, m<sup>2</sup>,

 a - specific surface of contact between air and water, m<sup>2</sup>/m<sup>3</sup>.

The basic resistance to oxygen transport through the system occurs in a liquid hence the total transport coefficient of oxygen by water  $(K_L)$ is approximately equal to the oxygen transport coefficient through water  $(k_L)$ .

Mass concentration of oxygen in air at the output, based on modified Henry's constant (*Hc*), is determined as follows:

$$c_{iz}=Hcc^*(c_{iz}).$$
 (3)

Modified Henry's constant (Hc), is determined by equation:

$$Hc = Ha/(R_uT_GC_L),$$
 (4)

where:

Ha- Henry's constant, Pa·kmol (O<sub>2</sub>+L)/kmol O<sub>2</sub>,  $R_u$ - the universal gas constant, J/(kmolK),  $T_G$ - absolute air temperature, K,  $C_L$ - molar concentration of oxygen in water,

C<sub>L</sub> - molar concentration of oxygen in water, kmol/m<sup>3</sup>.

Equations (3) and (4) give the expression for calculating the output mass concentration of oxygen in air:

$$c_{iz} = \frac{Ha(V_G c_{ul} + V_L k_L ac)}{V_G Ha + V_L k_L a(R_u T_G C_L)},$$
(5)

where:

k<sub>L</sub>a - coefficient of oxygen transport, 1/s.

Time dependence of dissolved oxygen concentration is presented by the following equation:

$$Y=mX$$
, (6)

where:

$$Y = \ln \frac{\frac{p_{ul}M_{O_{2}}}{R_{u}T_{G}} - \frac{Ha}{R_{u}T_{OK}C_{L}}c_{o}}{\frac{p_{ul}M_{O_{2}}}{R_{u}T_{G}} - \frac{Ha}{R_{u}T_{OK}C_{L}}c(\tau)},$$
(7)

m - slope coefficient of the equilibrium curve,

$$m = \frac{\frac{Ha}{R_u T_{OK} C_L} k_L a}{\frac{Ha}{R_u T_{OK} C_L} + \frac{V_L}{\dot{V}_G} k_L a} - R(\tau),$$
(8)

$$X = \tau$$
. (9)

The value of Y is given for each value of  $c(\tau)$  determined by experiments for defined time intervals.

The previous equations result in formulae for determining the coefficient of oxygen in wastewater as:

$$k_{L}a = \frac{Ha(m+R(\tau))V_{G}}{\dot{V}_{G} Ha - (m+R(\tau))V_{L}R_{u}T_{ck}C_{L}}$$
(10)

The coefficient of oxygen transport for standard conditions is determined in the following way [2]:

$$(k_{\rm L}a)_{\rm s} = \frac{(k_{\rm L}a)_{\rm t_{\rm L}}}{\theta^{\rm t_{\rm L}-20}},$$
 (11)

where:

 $(k_{\rm L}a)_{\rm t_{\rm L}}$  - experimentally obtained oxygen

transport coefficient, 1/s,

t<sub>L</sub> - water temperature, °C,

 $\theta = 1.024$  - temperature correction factor.

Based on the known value for the coefficient of oxygen transport  $(k_L a)_s$  the following technical characteristics of aeration systems for aeration of wastewater are calculated

[3]: actual capacity of oxygen introduction OC', actual efficiency of oxygen transport E' and actual energy efficiency of oxygen transport  $E_e'$ .

Actual capacity of oxygen introduction is calculated as the product of the standard capacity of oxygen introduction and corresponding correction factors that convert standard investigation conditions to real ones:

$$OC' = \alpha OC \frac{\beta c_h^* - c_o}{c_s^*} \theta^{(t_L - 20)}, \qquad (12)$$

where:

OC - standard capacity of oxygen introduction into wastewater, kg/h,

$$OC = (k_L a)_s c_s^* V_L$$

 $c_s^*$  - equilibrium mass concentration of dissolved oxygen in clean water, for standard conditions, kg/m<sup>3</sup>,

 $\alpha = 0.8 \div 0.94$  - relative transport degree of oxygen in wastewater,

 $\beta = 0.90 \div 0.97$  - relative saturation degree of wastewater with oxygen,

c<sub>h</sub>\* - equilibrium mass concentration of dissolved oxygen in clean water in actual conditions, corrected in relation to the height of the liquid column above the air distributor and molar participation of oxygen in air, mg/L,

$$c_{h}^{*} = c_{s}^{*} \left[ 1 + \frac{\rho_{L}g}{p_{n}} (H - h) \right]$$

p<sub>n</sub> - pressure corresponding to standard conditions, Pa,

H - total height of the water column, m,
 h - height from the bottom of the tank to the distributor, m,

 $\rho_L$  - water density, kg/m<sup>3</sup>.

The actual capacity of oxygen introduction OC' into wastewater should correspond to oxygen consumption during biological treatment.

The actual efficiency of the transport system is expressed in percentages and represents the ratio between the real capacity of oxygen introduction and the total oxygen flow brought by the aeration system [4]:

$$E' = \frac{OC'}{G_{O_2}} = \frac{OC'}{\left(\dot{V}_G\right)_n \rho_G y_{O_2}} \cdot 100,$$
(13)

where:

 $G_{O_2}$  - mass flow of oxygen introduced into the water by the aeration system, kg/h,

$$\left(\overrightarrow{V_{G}}\right)_{n}$$
 - volume air flow

(for  $p_n$ =101.3 kPa,  $t_L$  = 20°C), m<sup>3</sup>/h, ,  $\rho_G$  - air density for standard conditions

 $(t_{\rm G} = 20^{\circ}{\rm C}), \, {\rm kg/m^3},$ 

 $y_{O_2} = 0.232$  - mass participation of oxygen in air, kg/kg.

The real energy efficiency of oxygen transport represents the ratio between the actual capacity of oxygen introduction and the applied power needed to drive the aeration device:

$$E'_{e} = \frac{OC'}{\sum_{i} P_{i}},$$
(14)

where:

 $\sum_{i} P_{i}$  - sum of power off all electrical motors

(aerator, pump, blower, etc.), kW.

Based on all the experiments performed on the described installation for varying air flow between 2 and 10 m<sup>3</sup>/h and waste motor oil content from 0 to 10 mg/L using the investigated model  $(k_L a)_s$  values given in Table 2 were determined. The values obtained for  $(k_L a)_s$  were used to determine the values of actual capacity of oxygen introduction OC', real oxygen transport efficiency E' and actual energy efficiency of oxygen transport  $E_e$  also given in Table 2.

Technical characteristics of the aeration system in dependence on oil presence in wastewater, are given as diagrams in Fig. 2.

An increase of polluting components' concentrations (oil) in the water, led to a reduction of oxygen transport coefficient values and affecting other technical characteristics of the investigated aeration system.

Table 2. Technical characteristics of the aeration system for corresponding experimental regimes

Regime number	Waste oil concentration in water mg/L	(V <sub>G</sub> ) <sub>n</sub> m <sup>3</sup> /h	(k <sub>L</sub> a) <sub>s</sub>	OC' g/h	E' %	E <sub>c</sub> '
1	-	2.361	2.887	11.754	1.465	35.078
2	-	5.843	3.052	12.425	0.617	15.024
3	-	10.768	5.267	21.876	0.550	14.851
4	5	2.361	2.248	9.528	1.118	28.442
5	5	5.862	2.378	9.519	0.463	11.510
6	5	10.735	4.527	18.999	0.625	12.898
7	10	2.379	1.993	8.204	1.002	24.489
8	10	5.899	2.160	8.837	0.426	10.686
9	10	10.724	2.577	10.730	0.271	7.284

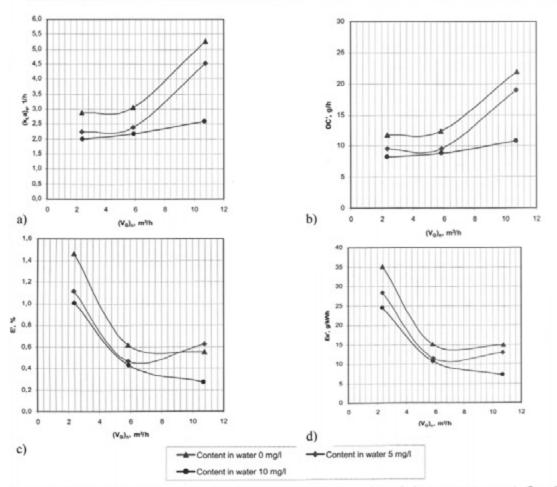


Figure 2. Influence of disc-shaped membrane air distributor's technical characteristics on air flow for different mass concentrations of oil in water (0; 5 and 10 mg/L)

a) coefficient of oxygen transport for standard conditions (k<sub>L</sub>a)<sub>s</sub>; b) actual capacity of oxygen introduction OC'; c) actual oxygen transport efficiency E'; d) actual energy efficiency of oxygen transport E'<sub>e</sub>

# 3 DEPENDENCY OF TECHNICAL INDICATORS ON THERMODYNAMIC INDICATORS AND PRESENCE OF OIL IN THE WATER DURING AERATION PROCESS

The law of energy balance can explain reduction of oxygen transport coefficient in the water during aeration with increasing waste oil concentration:

$$\frac{dE_{tot}}{d\tau} = \frac{dE_{kin}}{d\tau} + \frac{dE_{pot}}{d\tau}.$$
(15)

Change velocity of the total oxygen molar energy,  $E^{\Theta}_{tot}$ , is determined with oxygen transport coefficient,  $k_L a$  and influenced by the diffusion rate constant,  $k_d$ , the kinetic molar energy,  $E^{\Theta}_{kin} = \frac{3RT}{2}$ , as well as the adsorption rate constants,  $k_a$  in potential field through the free liquid surface, a [5]:

$$k_L a E_{\text{tot}}^{\Theta} = k_d 2 E_{\text{kin}}^{\Theta} + k_a E_{\text{pot}}^{\Theta},$$
 (16)

or in the form:

$$k_L a = k_d + (k_a / E_{tot}^{\Theta}) \Delta_{ads} G^{\Theta}$$
 (17)

The potential molar energy,  $E_{pot}^{\Theta}$  determined with oxygen bond strength, is equal with the oxygen molar adsorption Gibbs energy,  $\Delta_{ads}$   $G^{\Theta}$ , and can be affected by the presence of the oil oxidation products and radical initiators (OH, H<sub>2</sub>O<sub>2</sub>, Fe<sup>2+</sup>, HCO<sub>3</sub>/CO<sub>3</sub> <sup>2-</sup>, PO<sub>4</sub> <sup>3-</sup>, humid acids, aryl-R etc) [6]. Standard oxygen adsorption Gibbs energy in this work is determined with the Gibbs-Helmholtz - van t Hoff equation [7], applied for saturated water:

$$\mu(O_2)_{aq} = \mu(O_2)_g$$
. (18)

The chemical potential,  $\mu(O_2)$ , is determined with the standard value,  $\mu^{\theta}(O_2)$  and with oxygen concentration  $(c(O_2))$ :

$$\mu(O_2) = \mu^{\theta}(O_2) + RT \ln c(O_2).$$
 (19)

Determination of adsorption molar energy on the base the Equations (18) and (19) is performed using the obtained linear function (20):

$$\ln c(\mathrm{O_2})_{\mathrm{a}\,\mathrm{q}} = \, \ln c(\mathrm{O_2})_{\mathrm{g}} \, - \Delta_{\mathrm{ads}} \, G^\Theta \, (\mathrm{O_2}) / \mathrm{RT}, \ \, (20)$$

and presented in the Table 3 as:

$$y = y_o - \operatorname{tg} \varphi \cdot x$$
,

where:

 $y = \ln c \, (O_2)_{aq},$ 

 $y_0 = \ln c \, (O_2)_g$ 

$$\operatorname{tg} \varphi = \Delta_{\operatorname{ads}} G^{\Theta}(O_2) / R, \quad x = 1/T.$$

The calculated oxygen adsorption Gibb-s energies for the investigated regimes on the basis of the obtained linear functions to equation (21) are presented in the Table 4:

$$\Delta_{ads} G^{\Theta}(O_2) = R \cdot g \varphi$$
, (21)

The calculated oxygen kinetic parameters (the adsorption rate constants and diffusion rate constants) in aeration process:

$$k_a = 3RT \operatorname{tg} \varphi,$$
 (22)

$$k_{\rm d} = y_{\rm o} \,, \tag{23}$$

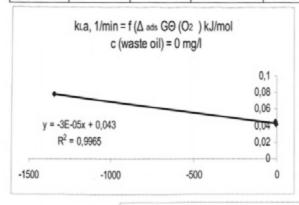
are presented in the Fig. 3 and the Table 5.

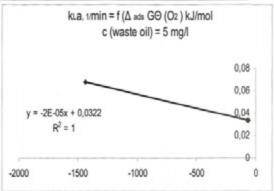
Table 3. Functions derived from the Equation (20) in conditions defined with c-h-q, c (oil concentration), mg/l, - h (height of water column), m, - q (air flow), m<sup>3</sup>/h

Investigated regimes defined with: c-h-q	$y = y_o - tg \varphi \cdot x$ were is to equation (20) $y = \ln c(O_{2,aq}) \text{ and } x = 1/T$	Coefficient correlation, R <sup>2</sup>	
0-2-2, 0-2-6, 0-2-10	y = -3663.1x + 4.4554	0.9219	
0-2-2, 0-2-6, 5-2-10, 5-1-6	y = 4367x - 23.624	0.9751	
0-2-10, 5-2-10, 10 -2-10	y = 165691x - 585.58	0.7455	
5-2-2 0-2-10, 5-1-2, 5-1-10	y = 8959.3x - 39.575	0.6137	
5-2-6, 10-2-2, 10-2-6	y = 7726.9x - 35.569	0.9939	
10-2-10, 10-1-2, 10-1-6, 10-1-10	y = 8492.3x - 38.096	0.9393	

Table 4. Thermodynamic and technical characteristics of examined regimes

Waste oil mg/L	(V <sub>G</sub> ) <sub>n</sub> m <sup>3</sup> /h	k <sub>L</sub> a 1/min	c (O <sub>2,l</sub> ) mg/dm <sup>3</sup>	T K	$\Delta_{ads} G^{\Theta}$ (O <sub>2</sub> ) kJ/mol	$\Sigma \Delta_{ads} G^{\Theta}$ (O <sub>2</sub> ) kJ/mol
-	2.361	0.0419	7.5	286	30.4 -36.3	-5.9
-	5.843	0.0443	7.6	286	30.4 -36.3	-5.9
-	10.768	0.0779	7.9	287	30.4 -1377	-1346
5	2.361	0.0339	6.4	288.0	-74.5	-74.5
5	5.862	0.0339	6.7	285.1	-64.2	-64.2
5	0.735	0.0677	7.0	287.5	-64.2 -1377	-1441.2
10	2.379	0.0292	5.9	286.7	-64.2	-64.2
10	5.899	0.0315	6.1	286.9	-64.2	-64.2
10	10.724	0.0382	6.4	287.1	-70.6 -1377	-1447.6
	oil mg/L - - 5 5 5	oil (V <sub>G</sub> ) <sub>n</sub> m <sup>3</sup> /h  - 2.361  - 5.843  - 10.768  5 2.361  5 5.862  5 0.735  10 2.379  10 5.899	oil mg/L $(V_G)_n$ m³/h $k_L a$ 1/min       -     2.361     0.0419       -     5.843     0.0443       -     10.768     0.0779       5     2.361     0.0339       5     5.862     0.0339       5     0.735     0.0677       10     2.379     0.0292       10     5.899     0.0315	oil mg/L $(V_G)_n$ m³/h $k_L a$ 1/min $c$ $(O_{2,l})$ mg/dm³       -     2.361     0.0419     7.5       -     5.843     0.0443     7.6       -     10.768     0.0779     7.9       5     2.361     0.0339     6.4       5     5.862     0.0339     6.7       5     0.735     0.0677     7.0       10     2.379     0.0292     5.9       10     5.899     0.0315     6.1	oil mg/L $(V_G)_n$ m³/h $k_L a$ 1/min $c$ $(O_{2,1})$ mg/dm³ $T$ K           -         2.361         0.0419         7.5         286           -         5.843         0.0443         7.6         286           -         10.768         0.0779         7.9         287           5         2.361         0.0339         6.4         288.0           5         5.862         0.0339         6.7         285.1           5         0.735         0.0677         7.0         287.5           10         2.379         0.0292         5.9         286.7           10         5.899         0.0315         6.1         286.9	oil mg/L $(V_G)_n$ m³/h $k_L a$ 1/min $c$ $(O_{2,1})$ mg/dm³ $T$ K $(O_2)$ kJ/mol           -         2.361         0.0419         7.5         286         30.4 -36.3           -         5.843         0.0443         7.6         286         30.4 -36.3           -         10.768         0.0779         7.9         287         30.4 -1377           5         2.361         0.0339         6.4         288.0         -74.5           5         5.862         0.0339         6.7         285.1         -64.2           5         0.735         0.0677         7.0         287.5         -64.2 -1377           10         2.379         0.0292         5.9         286.7         -64.2           10         5.899         0.0315         6.1         286.9         -64.2





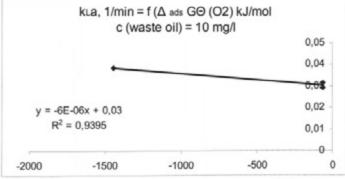


Figure 3. Diagrams obtained using Equation (17), for the regimes with the constant oil concentrations

Table 5. Theoretical values of the relaxation processes rate constants in the aeration system for

corresponding investigation regimes

Regime number	(V <sub>G</sub> ) <sub>n</sub> m <sup>3</sup> /h	$\Sigma \Delta_{diss} G^{\Theta}$ (O <sub>2 ,g/aq</sub> ) kJ/mol	k <sub>L</sub> a 1/min	k <sub>d</sub> 1/min	<i>k</i> <sub>0</sub> 1/min	1/τ <sub>m</sub> * 1/min	Compared measured with the calculated aeration rate constants
1	2.361	-5.9	0.0419	0.043	- 0.214	0.042	$     \frac{1/\tau_m = k_L a = k_d}{(1/\tau_m)/k_a = 0.19} $
2	5.843	-5.9	0.0443	44	. "	0.045	$ \frac{1/\tau_m = k_L a = k_d}{(1/\tau_m)/k_a = 0.21} $
3	10.768	1346	0.0779	"		0.048	$ \frac{1/\tau_m / k_L a = 0.62}{1/\tau_m / k_d = 1.11} \\ 1/\tau_m / k_a = 0.22 $
4	2.361	-74.5	0.0339	0.032	- 0.143	0.04	$(1/\tau_m)/k_L a = 1.17$ $(1/\tau_m)/k_d = 1.25$ $(1/\tau_m)/k_a = 0.28$
5	5.862	-64.2	0.0339	"	"	0.043	$(1/\tau_m)/k_L a = 1.27$ $(1/\tau_m)/k_d = 1.34$ $(1/\tau_m)/k_a = 0.3$
6	0.735	-1441.2	0.0677	"	"	0.053	$(1/\tau_m)/k_L a = 0.78$ $(1/\tau_m)/k_d = 1.65$ $(1/\tau_m)/k_a = 0.37$
7	2.379	-64.2	0.0292	0.03	-0.043	0.042	$(1/\tau_m)/k_L a = 1.42$ $(1/\tau_m)/k_d = 1.39$ $(1/\tau_m)/k_a = 0.97$
8	5.899	-64.2	0.0315	"	66	0.032	$(1/\tau_m)/k_L a = 1.4$ $(1/\tau_m)/k_d = 1.4$ $(1/\tau_m)/k_a = 1.0$
9	10.724	-1447.6	0.0382			0.053	$(1/\tau_m)/k_L a = 1.38$ $(1/\tau_m)/k_d = 1.75$ $(1/\tau_m)/k_a = 1.22$

<sup>\*</sup> measured period of aeration time enabling that constant oxygen concentration was achieved

The oxygen transport coefficient as technical indicator of aeration kinetic in correlation with the rate constants, obtained on the base of the thermodynamic study of aeration kinetic as in correlation with directly measured saturation time is presented in the Table 5.

In clean water, the oxygen transport coefficient is equal with the diffusion rate constant and with parameter calculated on the base saturation time ( $k_{\rm L}a=k_{\rm d}=1/\tau_{\rm m}$ ), but adsorption rate constants were five time greater,  $k_{\rm w}/(1/\tau_{\rm m})=4.8\div5.3$ . In the presence of added oil, relative adsorption rate constants were from  $3.6\div2.7$  for 5 mg/l oil concentration up to  $1.34\div0.82$  for 10 mg/L oil concentration. Equal adsorption rate constants with the saturation rate constants reduced aeration efficiency due to activated oxygen in the slow adsorption processes at 10 mg/L oil concentration.

### 4 CONCLUSION

Experimental research shows that 5 mg/L concentration of oil in the water, leads to reduction of the dissolved oxygen concentration from 10 to 15% compared to clean water, while 10 mg/L concentration of oil in the water reduces concentration of dissolved oxygen from 20 to 25% when compared to clean water. Aeration process technical indicators (oxygen introduction capacity, oxygen transport efficiency and energy efficiency of oxygen transport) for the clean water and water with 5 mg/L oil concentrations were significantly better with the maximum air flow, 10 m3/h, than with the less flow of 2 m<sup>3</sup>/h and 6 m<sup>3</sup>/h. For an oil concentration of 10 mg/L, the air flow of 10 m3/h did not have a significant influence on the aeration process technical indicators.

Based on the research of the dependence of technical indicators on thermodynamic parameters and presence of oil in the water during aeration process it can be concluded that:

- The oxygen transport coefficient is equal with the diffusion and saturation rate constants for clean water and contaminated water at the air flow of up to 6 m<sup>3</sup>/h.
- The oxygen transport coefficient for 10 m<sup>3</sup>/h air flow:
- is increased compared to diffusion rate constants 1.8 times and for water with 5 mg/L oil concentration 2.1 times for clean water
- is only 1.2, except for water with 10 mg/l oil concentration when the relative oxygen transport coefficient was compared to diffusion rate constants
- The study of the Gibbs energy adsorption dependence from oil concentrations shows:
- oxygen adsorption is activated with parallel endothermic and exothermic oxygen processes at the air flows up to 2 m³/h and 6 m³/h in the clean water,
- oxygen adsorption is activated with spontaneous, exothermic electrons transitions with the most adsorption affinity at the air flow of 10 m<sup>3</sup>/h in the contaminated water.
- Adsorption rate constants with increased oil concentrations become less negative and diffusion rate constants less positive values

of up to 10 mg/L oil concentration, when equal adsorption and saturation rate constants prevent the air flow influence on increasing the oxygen transport coefficient.

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