VOLUMETRIC COEFFICIENT OF OXYGEN MASS TRANSFER ANALYSIS IN A COLUMN PHOTOBIOREACTOR

Anatoliy Angelov, Evgeni Kraichev, Marta Lecheva, Sotir Plochev

University of Mining and Geology "St. Ivan Rilski", 1700 Sofia; tonyagev@mgu.bg

ABSTRACT. The oxygen mass transfer speed, as one of the technological factors influencing the growth and development of the phototrophic microorganisms (microalgae), was researched in a column type photobioreactor. A series of experiments under different aeration conditions were performed where the corresponding oxygen mass transfer coefficient values (K_La) were measured. The dynamics of basic technological parameters: temperature, pH, electrical conductivity etc. in parallel with the dissolved oxygen concentration were monitored. The oxygen mass transfer coefficient value influence during the different photosynthesis phases, as well as during the various phototrophic microorganisms' cultivation stages, was determined.

Keywords: volumetric coefficient of oxygen mass transfer, microalgues, photobioreactor and bioenergy

АНАЛИЗ НА ОБЕМНИЯ КОЕФИЦИЕНТ НА МАСОПРЕНАСЯНЕ ПО КИСЛОРОД В КОЛОНЕН ФОТОБИОРЕАКТОР

Анатолий Ангелов, Евгени Крайчев, Марта Лечева, Сотир Плочев

Минно-геоложки университет "Св. Иван Рилски", 1700 София

РЕЗЮМЕ. В колонен тип фотобиореактор е изследвана скоростта на масопренасяне на кислорода, като един от техологичните фактори оказващи влияние върху растежа и развитието на фототрофните микроорганизми (алги). Направени са серия от екперименти при различни условия на аерация, за които са измерени съответните стойноси на коефициента на масопренасяне по кислород (K_La). Проследена е динамиката на основни технологични параметри: температура, pH, електропроводимост и др., паралелно с концентрацията на разтворен кислород. Установено е влиянието върху стойността на коефициента на масопредаване по кислород (K_La), както през различните фази на фотосинтезата, така и през различните етапи от култивирането на фототрофните микроорганизми.

Ключови думи: Обемен коефициент на масопренасяне по кислород, алги, фотобиореактор и биоенергия

Introduction

One of the main factors for the successful functioning of gas-liquid reactors is the mass exchange in the gas-liquid system, which in turn depends on the hydrodynamic picture in the reactors, the phase mixing and the physico-chemical properties of the medium. Determination of the volume factor K_La in gas-liquid bioreactors is essential in order to determine the efficiency of aeration and to evaluate the effect of operating parameters on the oxygen supply to the system (Zedníková et al., 2018).

A major challenge is to develop a model that can well describe the physical nature of mixing in two-phase reactors, taking into account the influence of more parameters, and can be consistent with a wide range of experimental data. The contact between the two phases (liquid and gas) in the bioreactor depends mainly on its type, on the stirring speed and on the formation of gas bubbles.

Typically, the oxygen transfer rate is carried out over the entire contact surface (a) and refers to the working volume of the bioreactor. The driving force behind this process is the difference between the equilibrium and the current concentration of oxygen in the liquid phase (1):

$$\frac{dC_L}{dt} = k_L a\left(C_L^* - C_L\right) \quad (1)$$

The proportionality factor K_La is called the volumetric mass transfer coefficient of oxygen and plays an essential role in aerobic processes, C_L^* and C_L being the equilibrium and current oxygen concentrations, respectively. It is only measured indirectly, and depending on the environment - model or cultural. A number of authors (Law at al., 2004; Vandu, Krishna, 2004) have referred to the so-called "start-up dynamic method" as one of the most effective for determining K_La in bubble column reactors.

The use of microalgae for various purposes in biotechnology has attracted considerable scientific interest in recent decades because of its potential for use in wastewater treatment, biofuel production and valuable pharmaceutical products (Poonam & Sharma, 2017). The cultivation of microalgae can be carried out in open (natural and artificial lakes, lagoons, etc.) and in closed systems (photobioreactors - PBRs). Different type of photobioreactors (PBRs) are developed to optimise the various environmental factors and technological parameters (Wang et al., 2012).

Oxygenic photosynthesis (Masojídek et al., 2013) in microalgae includes the so-called. "Light" and "Dark reactions" and photorespiration (Fig. 1 and equation 2). Photosynthesis and respiration are processes that occur simultaneously in microalgae, but nonetheless, the rate of respiration is low compared to the rate of photosynthesis, leading to a net consumption of carbon dioxide and oxygen production. In the absence of light, algae respiration continues until photosynthesis stops, leading to net oxygen consumption and production of carbon dioxide (Masojídek et al., 2013; Malapascua et al., 2014).

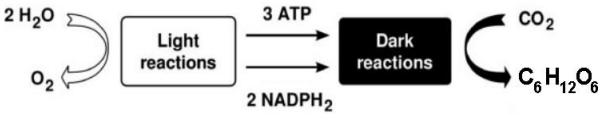

Fig. 1. Light and dark reactions of photosynthesis

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O + energy \qquad (2)$$

One of the important factors in the cultivation of microalgae is the balance between the concentrations of dissolved carbon dioxide and oxygen in the culture medium. Carbon dioxide concentration is vital for the growth and development of microalgae. The source of CO_2 for microalgae in autophototrophic culture can be a limiting factor if its concentration is low in the supply gas (for example, when only air is used as a source of CO_2). On the other hand, a high concentration of dissolved CO_2 would lead to a low pH of the culture medium, which may be inhibitory for some microalgae.

With respect to dissolved oxygen, some photobioreactors (eg Tubular and Serpentine PBRs) have been shown to accumulate oxygen and these higher levels of O_2 in the culture fluid can reduce the productivity of microalgae cultures. On the other hand, at high dissolved oxygen concentrations and high light levels, reactive oxygen species (ROS) can be formed, which can have a toxic effect on microalgae (Weissman et al., 1988).

The main objective of this study is to determine the effect on the value of the mass transfer coefficient for oxygen (K_La), both during the different phases of photosynthesis and during the different stages of cultivation of phototrophic microorganisms. At the same time, the dynamics of basic technological parameters are also monitored: temperature, pH and electrical conductivity, in parallel with the dissolved oxygen concentration in the bubble column PBR.

Materials and methods

To achieve these goals, the experiments were carried out in a laboratory installation (Fig. 2), including a bubble column PBR, representing a Plexiglas tube with an inside diameter of 85 mm, a height of 630 mm and a working volume of 2.5 dm^3. For efficient flow of photosynthesis along the PBR, a plexiglas tube with an internal diameter of 36 mm was installed in which a 20W fluorescent lamp - type "SunGlo" was installed in light illumination mode 12h light: 12h dark.

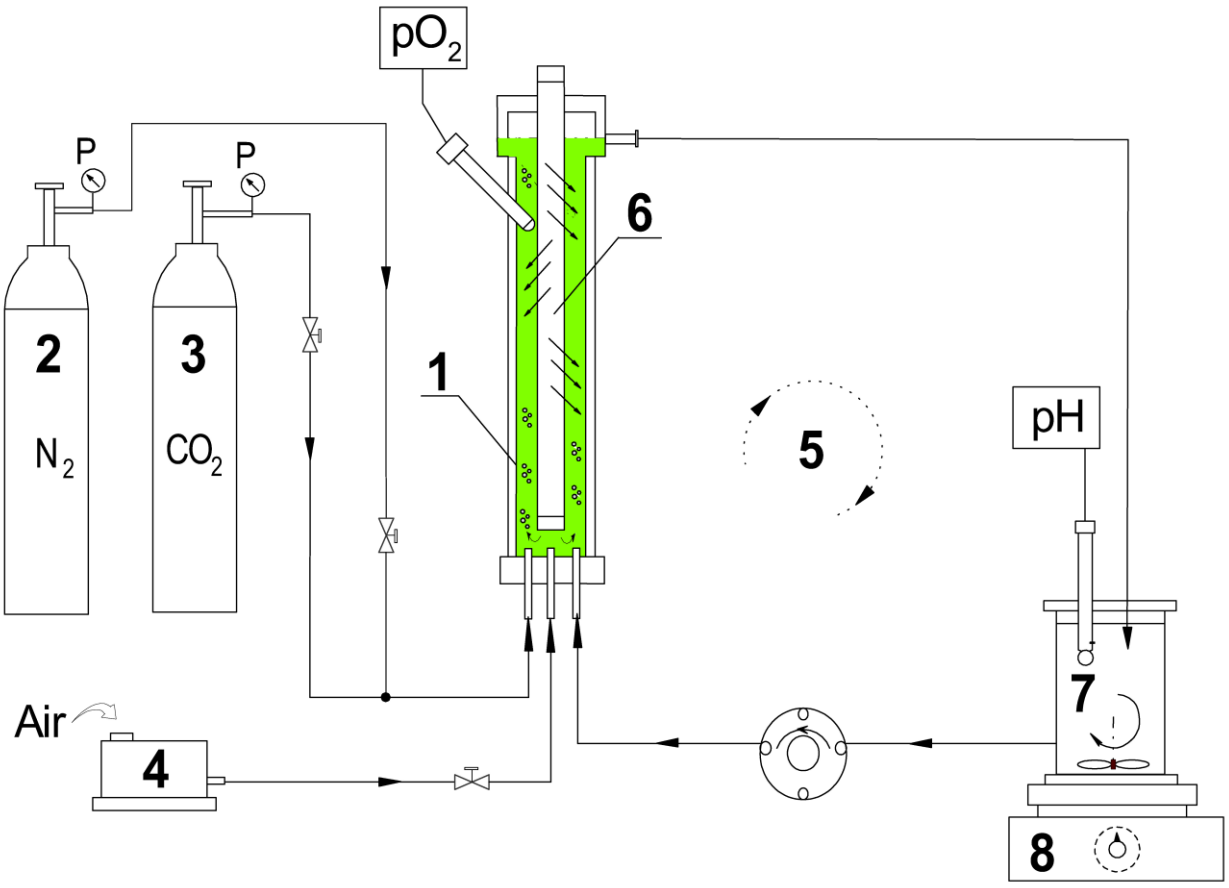

Fig. 2. Scheme of the laboratory installation: 1 - Photobioreactor (PBR), 2 - N_2 bottle, 3 - CO_2 bottle, 4 - Air pump, 5 - Recirculation pump, 6 - Fluorescent lamp, 7 - Buffer vessel, 8 - Magnetic stirrer

The culture fluid was recycled at a flow rate of 10 dm^3 / h by a peristaltic pump (5) through a buffer vessel (7) with a volume of 1 dm^3. From the bottom of the photobioreactor (PBR) through an air pump (4) the aeration was provided and a CO_2 bottle was used (3).

For laboratory testing Chlorella *sp*. algae strain (wild-type) was isolated from local freshwater. For the cultivation of microalgae, the modified medium BG-11 (Adriano et al., 2015) with the following composition was used for 1 L - 1.5 g $NaNO_3$, 0.5 g Na_2CO_3, 0.04 g K_2HPO_4, 0,075 g $MgSO_4.7H_2O$, 0.036 g $CaCl_2.2H_2O$, 0.045 g Citric acid, 0.0015 g, Ferric ammonium Citrate, 0.045 g EDTA (disodium salt), and 1ml trace elements solution consisted of 2.86 g/l H_3BO_3; 1.81 g/l $MnCl_2.4H_2O$; 0.222 g/l $ZnSO_4.7H_2O$; 0.39 g/l $NaMoO_4.2H_2O$; 0.079 g/l $CuSO_4.5H_2O$; 0.0494 g/l $Co(NO_3)_2.6H_2O$.

Algae were inoculated at 10% ($V_{inoculation}/V_{media}$) in a volume of 3.5 dm3 of PRB together with the buffer vessel (Fig. 2). Microalgae cultivation was carried out at room temperature in the range 23-25^{0}C. The photobioreactor (PBR) was aerated by means of an air pump with a flow rate of 2.5 dm^3/ h, without further addition of CO_2 to the air.

A variant of the start-up dynamic method based on the liquid phase oxygen balance (Vandu, Krishna, 2004) was used to determine the K_La mass transfer coefficient in the photobioreactor. For the purpose of measurement, constant aeration conditions are maintained in the column photobioreactor, whereby the dissolved oxygen concentration reaches a stationary value.

The process is as follows: initially dissolved oxygen dissolved in the liquid phase by purging the culture fluid with N_2 to reach dissolved oxygen content up to 0.1- 0.05 mg/l O_2. The system is then aerated again by passing purified air through the liquid (with an air flow rate of 2.5 dm^3/60 s), immediately measuring the dissolved oxygen concentration C_L over time (t) using an oxygen optic sensor - DO-BTA Vernier^R and using the LabQuest^R interface.

The measurements are continued until the equilibrium oxygen concentration is reached. The process is described by equation (1) and after its integration at t = 0, C_L* = const and $C_L = C_{L,0}$, assuming that at the beginning there is no oxygen in the liquid phase $C_{L,0}$= 0, we obtain:

$$\ln\left[\frac{C_L^*}{C_L^* - C_L}\right] = k_L a.t \qquad (3)$$

When plotted the graph - $\ln\left[C_L^* / \left(C_L^* - C_L\right)\right]$, as a function of time (t) and the slope of the obtained lines, the volume mass coefficient K_La is calculated.

A Burker counter with optical type microscope (Boeco BM-800) was used to determine the number of microalgae and parallel determination of the optical density (OD) of the cell suspension during microalgae cultivation was measured at 650 nm and a red filter. The laboratory facility provides on-line measurement of dissolved oxygen, pH, electrical conductivity, temperature and illumination by using Vernier^R BTA sensors and visualisation through the LabQuest^R interface.

Result and discussion

PBR work continued in the laboratory and samples from the culture suspension were taken to determine cell count and optical density (OD) during a period of 30 days. The results obtained in Fig. 3 show that the stationary phase was reached up to 20 days, with the exponential (Log) phase continuing between 5 and 20 days from the start of cultivation.

During the various stages of microalgae development, the value of K_La was measured (using the start-up dynamic method described above), at days 5, 15, and 25 respectively, during the dark and light phase of photosynthesis.

The dynamics of oxygen concentration for the three cases is shown on Fig.4. From the obtained results for the dynamics of dissolved oxygen, it can be concluded that the higher values of dissolved oxygen (in Light phase) in the medium during the exponential phase (15 days) are probably due to the more intense photosynthesis, respectively the production of photosynthetic oxygen.

At the beginning of the cultivation period (5 day), due to the lower intensity of photosynthesis, no significant differences in DO concentration were observed during the light and dark phases. At the end of the cultivation period (25 days), the equilibrium concentrations of dissolved oxygen C_L*, have values between the previous 2 cases (Fig. 4).

The results obtained with respect to the coefficient K_La (Table 1) for the 3 periods of cultivation in PBR, cannot be interpreted uniquely, but can serve to more effectively manage the aeration systems in this type of PBRs.

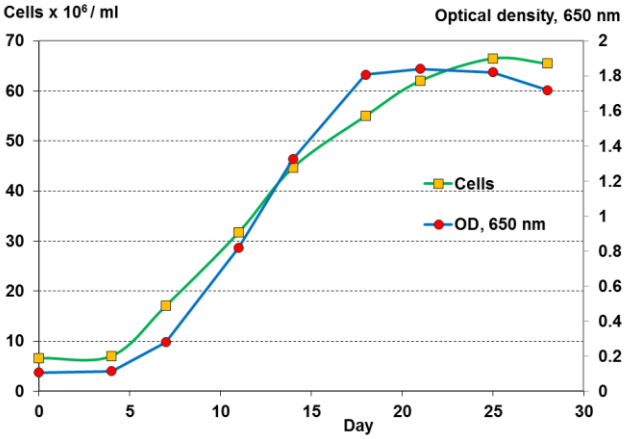

Fig.3. Growth curve and change in optical density (at 650 nm) in PBR

It should be borne in mind that the concentration of dissolved oxygen in the PBR, in addition to temperature, air flow rate and pressure (parameters which are kept constant), are influenced by the respiration rate and photosynthesis of microalgae, as well as the total dissolved solids (TDS), which increased from 1650 µS /cm to 2530 µS /cm (measured as electrical conductivity in the culture fluid) during PBR cultivation (30 days).

The calculated values of KLa (Table 1) showed variation in the range 0.0060 - 0.0067 s-1, which is confirmed by other studies conducted in bubble column PBR (Kazbar et al., 2019). The relative difference of KLa values between the light and dark phases is greatest in the measurements taken on the 15th day from the beginning of the experiment, i.e. during the exponential (Log) phase.

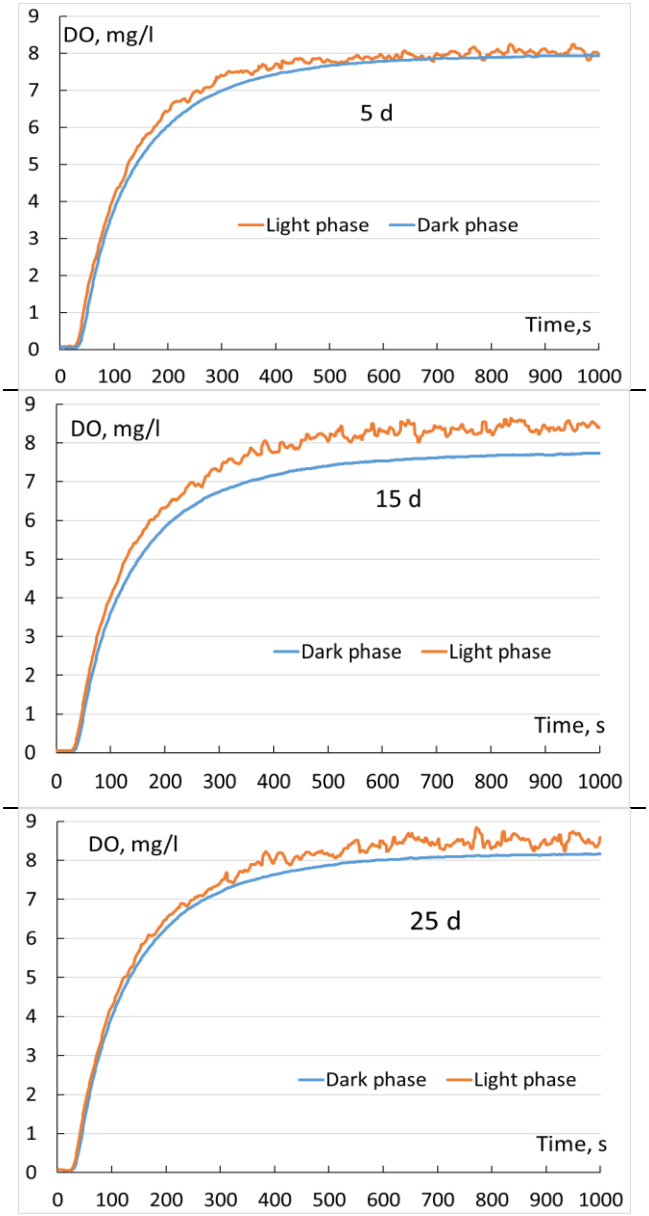

Fig. 4. The dynamics of dissolved oxygen in determining K_La for 5, 15 and 25 days of microalgae cultivation

Table1. *Values of K_La at 5th, 15th and 25th days of microalgae cultivation*

Day	5	15	25
K_La, s^{-1}			
Dark phase	0.0060	0.0061	0.0068
Light phase	0.0062	0.0066	0.0071

Table2. *K_La values at different air flow rates in the PBR*

Q, L/min	1.0	2.5	4.5
K_La, s^{-1}			
Dark phase	0.0061	0.0063	0.0083
Light phase	0.0062	0.0068	0.0084

In the studies performed to determine the influence of the degree of aeration (for 3 different air flow rates) on the value of K_La, an increase from 0.061 to 0.084 s^{-1} was found during both phases of photosynthesis (Table 2 and Fig. 5). These measurements were performed till the end of the microalgae cultivation in the period (day 30) in PBR.

Undoubtedly, the optimisation of the aeration system and the hydrodynamics of the flow in the bubble column PBR are likely to have a positive effect on the production of microalgae biomass. During the various stages of PBR operation, no accumulation of high oxygen levels in the reactor volume was detected.

For a more detailed study of the photosynthesis and respiration processes of microalgae in PBRs, it is necessary to consider both mass transfer and CO_2 (Kazbar et al., 2019), as well as the ratio of mass transfer rates for CO_2 and O_2 - K_La (CO_2) / K_La (O_2).

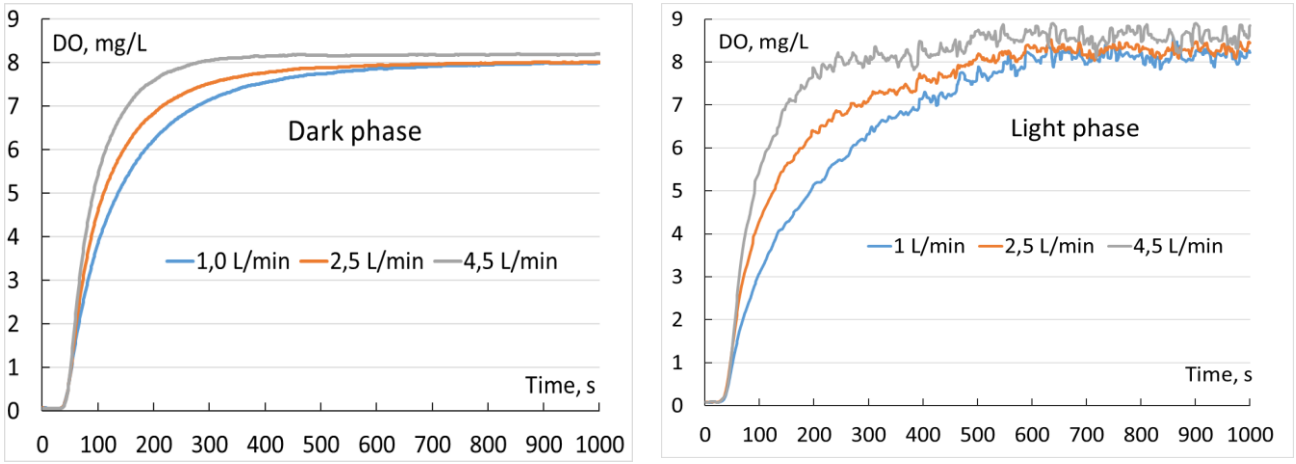

Fig. 5. Dynamics of dissolved oxygen during the determination of K_La, for different flow rates of the supplied air

Conclusion

In the present bubble column PBR study, the rate of oxygen mass transfer was examined as one of the technological factors affecting the growth and development of microalgae. The values of K_La in the real culture medium have been established, both during the different phases of photosynthesis and during the different stages of cultivation of phototrophic microorganisms. The results obtained can serve to optimise microalgue cultivation processes and refine PBR design.

Acknowledgment. This study was fundedby the Bulgarian National Science Fund, Grant № KP_06_ H27/4, 08.12.2018.

References

Adriano, A. H., M. da R. Gabriel, M. Luiza, G. de M. Michele, A. V. C. Jorge. 2015. The cultivation of microalgae Cyanobium sp. and Chlorella sp. in different culture media and stirring setting. – *African Journal of Microbiology Research*, 9, 21, 1431–1439.

Kazbar, A., G. Cogne, B. Urbain, H. Marec, B. Le-Gouic, J. Tallec, J. Pruvost. 2019. Effect of dissolved oxygen concentration on microalgal culture in photobioreactors. – *Algal Research*, *39*, 101432.

Lau, R., W. Peng, L. G. Velazquez-Vargas, G. Q. Yang, L. S. Fan. 2004. Gas−Liquid Mass Transfer in High-Pressure Bubble Columns. – *Industrial & Engineering Chemistry Research*, *43*, 5, 1302–1311.

Malapascua, J. R. F., C. G. Jerez, M. Sergejevová, F. L. Figueroa, J. Masojídek. 2014. Photosynthesis monitoring to optimise growth of microalgal mass cultures: application of chlorophyll fluorescence techniques. – *Aquat. Biol., 22*, 123–140.

Masojídek, J., Torzillo, G., Koblížek, M. 2013. Photosynthesis in Microalgae. Handbook of Microalgal Culture, 21–36.

Poonam Sharma, Nivedita Sharma. 2017. Industrial and biotechnological applications of algae: A review. – *Journal of Advances in Plant Biology*, *1*, 1, 1–25.

Vandu, C. O., R. Krishna. 2004. Influence of scale on the volumetric mass transfer coefficients in bubble columns. – *Chemical Engineering and Processing: Process Intensification*, *43*, 4, 575–579.

Wang, B., C. Q. Lan, M. Horsman. 2012. Closed photobioreactors for production of microalgal biomasses. – *Biotechnology Advances, 30*, 4, 904–912.

Weissman, J. C., R. P. Goebel, J. R. Benemann. 1988. Photobioreactor design: Mixing, carbon utilization, and oxygen accumulation. – *Biotechnology and Bioengineering, 31*, 4, 336–344.

Zedníková, M., S. Orvalho, M. Fialová, M. Ruzicka. 2018. Measurement of volumetric mass transfer coefficient in bubble columns. – *Chem. Engineering, 2*, 2, 19.