

# Determination of wastewater mass transfer coefficients for methane in a Gas/Liquid-Batch reactor

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## Abstract

In order to minimize uncontrolled methane emissions from anaerobic municipal waste water treatment systems into the atmosphere, recently adapted UASB reactor operating strategies and gas recovery measures are being developed. Therefore mass transfer processes of methane in water (formation and solubility), via the water surface (phase transition) into the gas phase (emission) have been investigated. In the literature, only few data are available for methane mass transfer coefficients ( $k_{La}$ ) in anaerobic digestion systems or real wastewaters. For this purpose a sorption and desorption test of methane in pure water and in wastewater has been developed and implemented to derive water-specific  $k_{La}$  values considering temperature, turbulences and water quality (e.g. salinity, surfactants, etc.). From the preliminary experiments carried out so far it can be stated that the developed methodology is adequate to measure robust data and, that the method is validated by good agreement between observed and estimated mass transfer and diffusion coefficients of methane and oxygen. A provisional temperature coefficient based on a van't Hoff-Arrhenius relationship of 1,017 is determined for a temperature range of 25°C to 35°C. The influence of the volume specific energy input (P/V) on the  $k_{La}$  can be described by adaptation of, a method used to determine the volatilization of volatile organic compounds in surface aeration reactors.

## Keywords

Anaerobic waste water treatment, methane emissions, mass transfer coefficient, dissolved methane

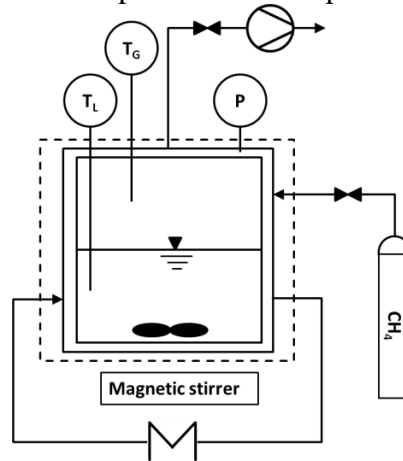
## INTRODUCTION

In hot climatic zones, anaerobic wastewater treatment constitutes a viable alternative to the conventional aerobic treatment of municipal wastewater. The process has low power consumption while also generating methane, which can be used to produce energy, and the treated wastewater is suitable for use in agricultural irrigation, as plant nutrients are not eliminated. An aspect that is disadvantageous to the system's impact on the climate is the fact that a certain portion of the greenhouse gas methane remains dissolved in the effluent, from where it can escape into the atmosphere in an uncontrolled fashion (Souza et al., etc.). To minimize this effect recently adapted UASB operating strategies and gas recovery measures are being developed. The basis for this is the study of the mass transfer processes of methane in water (formation and solubility of methane), via the water surface (phase transition) into the gas phase (emission). In the literature, only few data for methane mass transfer coefficients ( $k_{La}$ ) in anaerobic digestion systems are available. *Pauss et al.* (1990) estimated  $k_{La}$  values for methane from three different methanogenic reactors for a wide range of mixing and gas production conditions. Moreover the obtained coefficients were estimated based on measurements of dissolved and gaseous hydrogen concentrations. For the Sludge Bed Reactor the reported values range from 0,02 1/h at 32°C to 0,23 1/h at 35°C. Furthermore these data do not allow a differentiated consideration of the impact of temperature, turbulences and operational conditions e.g. sludge accumulation on the water/gas interface. For this purpose a sorption and desorption test for methane in pure water and in wastewater has been developed and implemented to derive water-specific mass transfer coefficients considering turbulences, temperature and water quality (e.g. salinity, surfactants, etc.).

## MATERIAL AND METHODS

### Experimental set up

This study was conducted in a Gas/Liquid-batch reactor consisting of double wall Plexiglas® reactors with a working volume of 3,5 L (Figure 1). A controlled agitation of the water phase was achieved inside the reactor by means of a magnetic stirrer which could be regulated between 0 and 600 RPM. The temperature within the reactors was controlled via thermostat and circulating refrigerant. The measurement of the liquid and the gas temperature was carried out by a thermocouple in the gas as well as the aqueous phase. An integrated pressure sensor, a vacuum pump and heat insulation completed the experimental set-up.



**Figure 1.** Schematic diagram of the Gas/Liquid-batch reactor

### Methodology

In this experiment the physical sorption and desorption velocity of methane in water is determined under constant temperature conditions in a closed system. Using equation (1), which can be derived from the two-film Theory of Gas Transfer, the change of concentration of dissolved methane, caused by the mass transfer through the surface of a liquid bulk phase, can be computed with respect to time:

$$c_L(t) = c_s - (c_s - c_0) * \exp(-K_L a * t) \quad (1)$$

with  $k_L a$  = volumetric mass transfer coefficient [1/];  $c_s$  = concentration in equilibrium with gas derived by Henry's law [mg/L];  $c_L(t)$  = concentration in liquid bulk phase at time  $t$  [mg/L]; and  $c_0$  = concentration in liquid bulk phase at the beginning of measurement ( $t = 0$ ) [mg/L].

At the beginning of the test a defined amount of water is added to the reactor and then evacuated for several minutes by means of a vacuum pump in order to achieve a removal of dissolved air and an emptying of the gas space. After degassing the reactor internal pressure is approximately equal to the vapor pressure of the water. Afterwards, the gas space of the reactor is filled with pure methane until a defined pressure level is reached in order to supply a defined quantity of methane.

The resulting pressure reduction due to the dissolving of the methane in water is registered continuously over time. Using the ideal gas law, the mass transfer rate can be calculated. Furthermore using formula (1) and non-linear regression the  $k_L a$  coefficient can then be determined.

## RESULTS

### Specific transfer coefficient as a function of temperature and the specific energy input

According to *Hsieh et al.* (1993), a correlation between the specific energy input and a surface aerator can be expressed as follows

$$(P/V) = a * (N)^b \quad (2)$$

with  $P/V$  = specific power input [W/m<sup>3</sup>];  $N$  = rotational speed [RPM];  $a$  and  $b$  = correlation factors

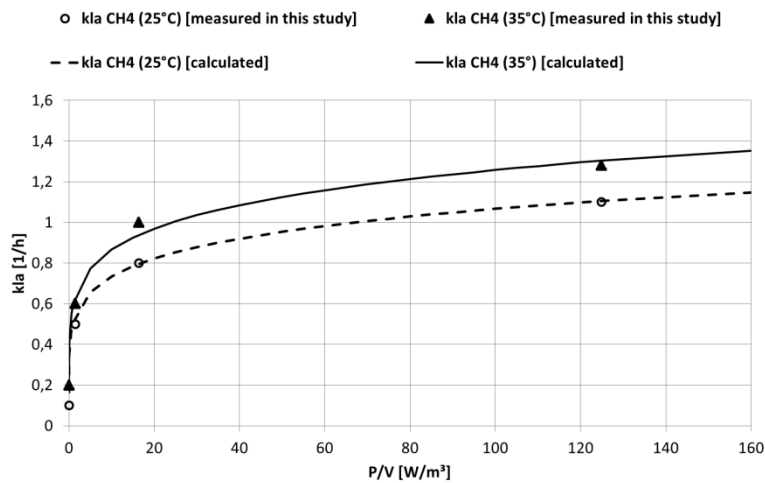
[-]. For the system considered here, the same approach for the description of the specific energy input is used as a function of rotational speed. The power introduced into the water is estimated from the measured rotational speed of the water mass. Furthermore the  $k_L a$  coefficient is dependent on the temperature. This relationship can be expressed by an adaptation of the van't Hoff-Arrhenius equation to the given conditions

$$k_{L}a_T = k_{L}a_{T_{35}} * \theta^{(T-35)} \quad (3)$$

with  $k_{L}a_T$  = volumetric mass transfer coefficient at temperature T [1/h]; reference volumetric mass transfer coefficient at 35°C [m/h];  $\theta$  = temperature coefficient [-]; T = temperature [°C]. Finally the overall  $k_L a$  coefficient can be computed combining equation (2) and (3) as follows

$$k_{L}a (T, P/V) = \left[ \frac{A}{V} \right] * [P/V] * [\theta^{(T-35)}] \quad (4)$$

Where  $k_L a (T, P/V)$  = volumetric mass transfer coefficient [1/h]; A = surface through which mass is transferred [m<sup>2</sup>]; V = volume in which gas is dissolved [m<sup>3</sup>].



**Figure 2.** Measured and calculated  $k_L a$  values as a function of P/V input at T = 25°C and T = 35°C

Using non-linear regression, correlation coefficients  $a= 0,597$  and  $b = 0,162$  and the temperature coefficient  $\theta=1,017$  is obtained. Moreover Figure 2 underlines that the influence of water temperature and the specific energy input on the  $k_L a$  coefficient can ideally be described by equation 4. .

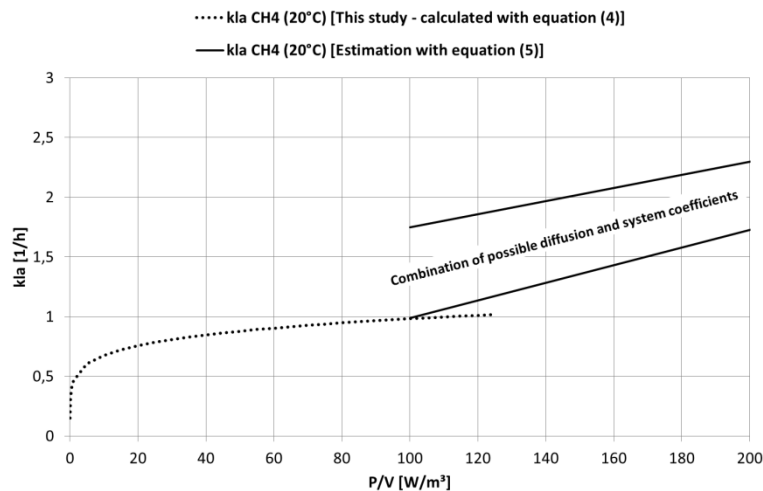
### Validity test

According to *Metcalfe & Eddy* (2003) several experimental studies confirmed that the  $k_L a$  coefficient can be estimated by the ratio of the system's diffusion coefficients as follows:

$$k_{L}a_{VOC} = k_{L}a_{O_2} * \left( \frac{D_{VOC}}{D_{O_2}} \right)^n \quad (5)$$

with  $k_{L}a_{VOC}$  = VOC mass transfer coefficient in the system [1/h];  $k_{L}a_{O_2}$  = oxygen mass transfer coefficient in the system [1/h];  $D_{VOC}$  = diffusion coefficient of VOC in water [cm<sup>2</sup>/s];  $D_{O_2}$  = diffusion coefficient of oxygen in water [cm<sup>2</sup>/s]; n = system coefficient [-].

Figure 3 depicts methane  $k_L a$  values estimated corresponding to equation 5 using  $k_L a$  for oxygen at 20 °C with P/V > 100 W/m<sup>3</sup> reported by *Hsieh et al.* (1993) and diffusion coefficients compiled in *Landolt-Börnstein* (2007). The summarized diffusion coefficients at 20 °C of methane vary from 1,47 to 2,4 m<sup>2</sup>/s and of oxygen from 2,12 to 2,30 m<sup>2</sup>/s. The coefficient n is system specific and can range normally between 0,5 and 1,0. e.g. for surface aerators and a specific energy input lower than 100 W/m<sup>3</sup>, n = 0,5 can be estimated.



**Figure 3.** Measured and calculated  $k_{L,a}$  values as a function of  $P/V$  input at  $T = 25$  and  $T = 35^{\circ}\text{C}$

From Figure 3 it can be seen that with a  $P/V$  of around  $100 \text{ W/m}^3$  the  $k_{L,a}$  values measured in this study and predicted with equation 4 are in the same range as the estimated  $k_{L,a}$  values using equation 5. Thus it can be assumed that the developed method produces plausible results.

## CONCLUSIONS

A method has been developed and implemented to derive  $k_{L,a}$  coefficients for methane in pure water and in wastewater considering  $P/V$  input and temperature. From the preliminary experiments carried out so far, it can be stated that the developed methodology is adequate to measure the necessary data and the method has been validated by good agreement between observation and estimating methane mass transfer coefficients from oxygen  $k_{L,a}$  and from methane and oxygen diffusion coefficients. A provisional temperature coefficient based on a van't Hoff-Arrhenius relationship of 1,017 was determined for a temperature range of  $25^{\circ}\text{C}$  to  $35^{\circ}\text{C}$ . The influence of the volume specific energy input ( $P/V$ ) on the  $k_{L,a}$  can be described by adaptation of a method used to describe volatilization of volatile organic compounds in surface aeration reactors. The Gas/Liquid batch-reactor will be used in further trials to determine, analogous to aeration tests, salinity and interfacial coefficients. Furthermore waste-water specific saturation concentrations, considering the chemical composition, will be determined.

## ACKNOWLEDGEMENTS

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## REFERENCES

- Hsieh, C., Ro, K. S., Stenstrom, M. K. (1993): Estimating Emissions of 20 VOCs II, Diffused Aeration. *Journal of Environmental Engineering* vol 119, no. 6, pp 1099-1118.
- Landolt-Börnstein (2007): Numerical Data and Functional Relationships in Science and Technology, Group IV: Physical Chemistry, Volume 15 Diffusion in Gases, Liquids and Electrolytes. *Springer-Verlag*, Berlin, New York.
- Metcalf and Eddy, Inc. (2003): Wastewater Engineering – Treatment and Reuse, 4th Edition. *McGraw-Hill*, New York.
- Pauss, A., Andre, G. Perrier, M., Guiot S. R. (1990): Liquid-to-Gas Mass Transfer in Anaerobic Processes: Inevitable Transfer Limitations of Methane and Hydrogen in the Biomethanation Process. *Applied Environmental Microbiology*. 56(6):1636.