Singlet molecular oxygen application for 2-chlorophenol removal

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Abstract

A special kind of photocatalysis—a photosensitized oxidation involving singlet molecular oxygen ($^1O_2$) was applied to decomposition of 2-chlorophenol (2-CP) in water solution. The photoprocess was carried out in a homo- and heterogeneous system using rose bengal (RB) as a sensitizer. In the homogeneous solution the influence of initial 2-CP concentration and pH on reaction rate was observed. Based on the kinetic model, the rate constants of $^1O_2$ quenching and reaction with 2-CP and the rate constant of excited sensitizer quenching by 2-CP were determined. In the heterogeneous system, silane gel was a carrier for the immobilized sensitizer. In order to estimate kinetic parameters, an attempt was made to describe the process using Langmuir–Hinshelwood (L–H) type mechanism. The Langmuir equilibrium constants for oxygen and 2-CP adsorbed on the gel surface were also estimated.
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1. Introduction

The photosensitized oxidation consists in using a particular kind of catalyst—sensitizer. During photosensitization process, the sensitizer absorbs light and is excited to a higher energy state, firstly to the singlet state and then, through the intersystem crossing to the triplet state. The excited triplet state of the sensitizer can transfer energy to ubiquitous molecular oxygen producing singlet molecular oxygen. The excited sensitizer can also participate in electron transfer process often initiating radical reactions [1,2].

The main advantage of photooxidation with dye sensitizers is the use of two ubiquitous resources: solar photons in the visible range for dye photoexcitation and oxygen from air. For this reason the photosensitized oxidation occurs in nature, participating to some extent in the restoration of equilibrium in the destroyed environment [3,4].

Drawbacks of this process are low photostability of the sensitizers and difficulty in removing them from the reaction mixture after finishing the process. These problems can be overcome by the application of a new generation of sensitizers, more resistant to autodegradation, in immobilized state [5–7].

The kinetics of pollutant degradation in the heterogeneous systems is usually described by the Langmuir–Hinshelwood (L–H) type approach. In the field of the environmental protection, this approach has been presented by many authors [8–10]. These works usually refer to the photocatalytic process with TiO_2 as a catalyst. The use of L–H kinetics to the description of photocatalysis enables determination of kinetic parameters that are not connected directly with the Langmuir adsorption isotherm constants, or with traditional L–H constants used in the reactions with a solid catalyst [11]. Therefore, a physical meaning of the parameters obtained is different. Actually, there are experimental constants describing the rate of degradation in definite experimental conditions and true for a definite range of substrate concentrations. However, some authors [8,9] try to relate more or less the experimental parameters to adsorption constants, and even to fix their relationships with elementary consequential reactions resulting from the reaction mechanism [12]. According to our knowledge, the photosensitized oxidation with an immobilized sensitizer has not been analyzed yet from the point of view of a kinetic description.

The goal of this work was to investigate the oxidation of 2-chlorophenol (2-CP) using photoexcited rose bengal (RB) in a homogeneous aqueous solution and with a sensitizer immobilized on water nonsoluble carrier. 2-Chlorophenol was chosen as a model representative organic pollutant belonging to chlorophenolic compounds which are widely used in industry and daily life and have caused considerable damage and threat to the
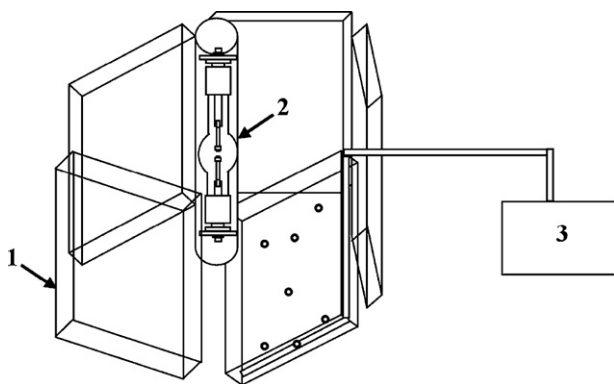
Fig. 1. Schematic of the system of plate reactors used in bench-scale experiments: (1) plate reactor, (2) xenon lamp, and (3) peristaltic pump.

ecosystem in aquatic bodies and human health. Studies in this field can help clearing up and understanding self-repairing processes that take place in water reservoirs.

2. Materials and methods

Rose bengal disodium salt, 2-CP (98%) and potassium Reinecke's salt were purchased from Fluka. Tetraethylorthosilicate (TEOS) was purchased from SIGMA.

Studies were carried out for various initial 2-CP concentrations at two pH values: 6 and 10.3, at which in water solution there is practically only undissociated 2-CP and 2-CP anion, respectively. The experiments were run in phosphate buffered solutions (NaH_2PO_4–K_2HPO_4; both at concentration 0.1 M (p.a. POCH, Poland)) at pH 6 and in carbonate buffer (Na_2CO_3–$NaHCO_3$, both at 0.05 M (p.a. POCH, Poland)) for pH 10.3. All reaction solutions were prepared in distilled water additionally treated in Millipore Milli-Q Plus system.

The experiments were performed in a semibatch system in the series of flat plate reactors built of two plates 6×10 cm made from sodium glass (Fig. 1).

The reaction mixture ($0.01 \, dm^3$) was aerated and agitated by gas bubbling. In the homogeneous system, a solution contained 2-CP, RB and a buffer, in the heterogeneous one, the inner surfaces of two plates were covered by gel with the immobilized dye sensitizer. The reactors were placed around a xenon arc lamp of the electrical power 100 W (Osram). The emission spectrum of this lamp simulated solar radiation. The quantity of absorbed photons was calculated using Reinecke's actinometer for wavelengths ranging from 310 to 770 nm [13]. The calculated photon flux entering the reaction space for majority of experiments amounted to 3.33×10^{18} quanta/s.

In heterogeneous experiments, a sensitizer (RB) was immobilized in silane gel based on TEOS. The sol was made by sol–gel technique. The details of sol composition and the gel preparation procedure were described earlier by Gryglik et al. [14].

The 2-CP decay was monitored by HPLC apparatus (Waters) with a photodiode array detector, equipped with Symmetry C18 column. A mixture of $MeOH:H_2O$ (vol. 1:1) at the constant flow rate equal to 0.8 ml/min was used as an eluent.

3. Results and discussion

3.1. The homogeneous system

The 2-CP decay in the studied system can proceed along three pathways: (1) the reaction of direct photolysis, (2) the reaction with singlet oxygen and (3) 2-CP decay in a radical pathway initiated by its reaction with excited RB.

Analyzing the emission spectrum of the xenon lamp and absorption spectrum of 2-CP and 2-CP anion (Fig. 2A), one can suspect that direct photolysis in the photodegradation process of 2-CP cannot be disregarded. The obtained experimental data (Fig. 2B) confirmed this suspicion.

As can be seen in Fig. 2B, the direct photolysis of 2-CP under xenon lamp illumination can appear to a very small extent in neutral solutions and at the highest rate, it can occur in an alkaline solution. However, the presence of RB caused an increase of the rate of 2-CP decay in comparison with direct photolysis, especially at pH 10.3.
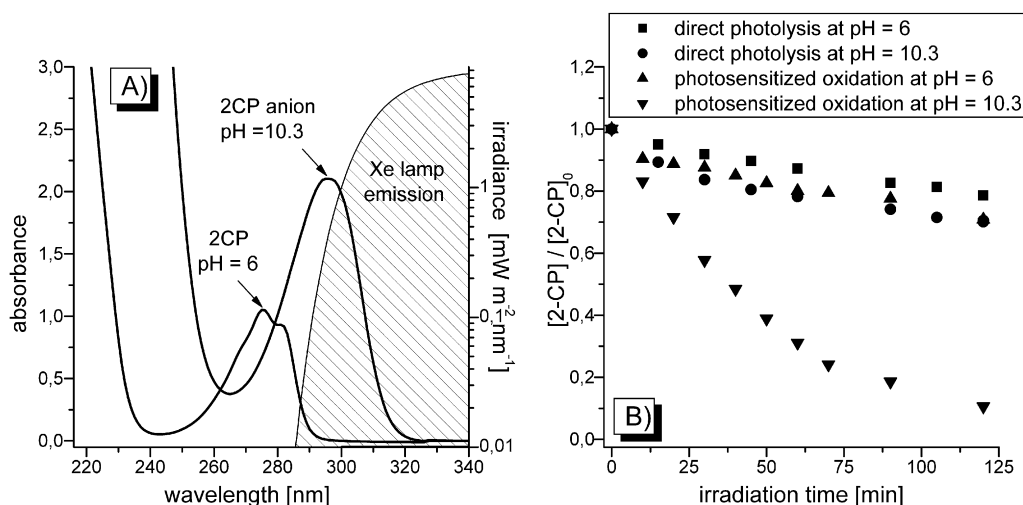

Fig. 2. (A) The absorption spectra of 2-CP ([2-CP] = 5×10^{-4} mol dm^{-3}) at pH 6 and 10.3 against the background of Xe 100 W lamp emission. (B) Comparison of 2-CP concentration changes ([2-CP]$_0$ = 5×10^{-4} mol dm^{-3}) caused by direct photolysis and photosensitized oxidation with RB as a sensitizer at pH 6 and 10.3.

Experiments with commonly used $^1O_2$ quencher—sodium azide (NaN_3) excluded a possibility of radical reactions, so we assumed that a prevailing reaction in the 2-CP decay was the reaction with singlet oxygen. In such a case, assuming the lack of direct photolysis, the rate of 2-CP decay (r), is given by the following equation:

$$r = -\frac{d[2\text{-CP}]}{dt} = k_r[^1O_2][2\text{-CP}] + k_r'[^1O_2][2\text{-CP}^-] \qquad (1)$$

where k_r is the rate constant of $^1O_2$ reaction with 2-CP in neutral solution and k_r' is respectively the rate constant in alkaline solution.

After several simplifications [15], the mechanism and kinetic model of the process were established giving finally the following relationship:

$$r = -\frac{d[2\text{-CP}]}{dt} = \frac{\phi_\Delta I_a k_r[2\text{-CP}]}{(k_d + k_t[2\text{-CP}])(1 + k_Q^{2CP}[2\text{-CP}]/k_Q^{O_2}[O_2])} \qquad (2)$$

where k_r is the rate constant of $^1O_2$ reaction with 2-CP, $k_t = k_r + k_q$ where k_q is the rate constant quenching of $^1O_2$ by 2-CP, and $k_Q^{2\text{-CP}}$, the rate constant of excited triplet RB quenched by 2-CP.

It should be noted that Eq. (2) in a generalized form can be simplified to Eq. (3) when the excited sensitizer is weakly quenched by the molecule of interest in comparison with triplet oxygen quenching, i.e., when quotient in the denominator is much smaller than one.

$$r = -\frac{d[2\text{-CP}]}{dt} = \frac{\phi_\Delta I_a k_r[2\text{-CP}]}{(k_d + k_t[2\text{-CP}])} \qquad (3)$$

The relationship (3) was usually applied to describe the kinetics of sensitized oxidation [5,16,17].

The application of Eq. (2) in the initial period of reaction allowed us to estimate three kinetic parameters: k_r, k_q and $k_Q^{2\text{-CP}}$. Table 1 gives results of the calculations and Fig. 3 shows a comparison of experimental data for neutral and alkaline solution with theoretical course according to Eq. (2). The values of rate constant of $^1O_2$ decay in water, k_d and quantum yield of $^1O_2$ formation ϕ_Δ were taken from literature [18].

The initial reaction rates were calculated by differentiation of the 2-CP decay curve which fitted experimental points ([2-CP], t) at a correlation coefficient higher than 0.96. The values of reaction rate for various pH were diminished by the values of direct photolysis rates.

The observed higher rate of 2-CP degradation in alkaline solutions follows from a higher rate constant of chlorophenolate anion reaction with $^1O_2$ [19]. Chlorophenol anions are also effi-
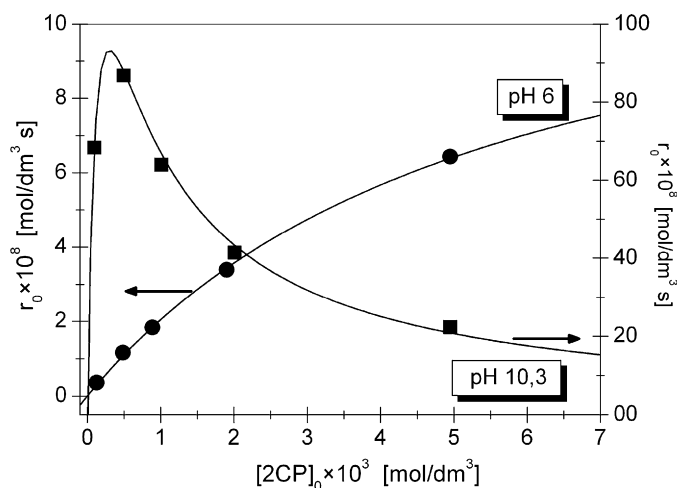

Fig. 3. Dependences of the initial reaction rate at pH 6 and 10.3 upon initial 2-CP concentration, lines are the theoretical course according to Eqs. (2) and (3), points are the experimental results.

cient in physical deactivation of singlet oxygen, thus strongly competing with chemical reaction [17]. The calculated rate constants of $^1O_2$ reaction with 2-CP and 2-CP anion agree well with literature data [19,20] and our earlier work [15] which confirms the simplification and assumption made in the kinetic model.

The obtained high value of quenching rate constants of excited RB by 2-CP and its anion ($k_Q^{2\text{-CP}}$) and the lack of radical reaction indicate that significant part of RB is not employed for $^1O_2$ generation.

Despite many advantages, the homogeneous process needs separation of the photocatalyst from the solution after the reaction. Thus, we decided to continue our investigations using a dye in the immobilized form, especially that the heterogeneous process was characterized by higher efficiency of 2-CP degradation in water solution [14].

3.2. The heterogeneous system

In typical L–H kinetics, it is assumed that reacting substances can adsorb themselves in the same active spots on the surface and one of the reagents can move along the surface. If a surface reaction determines the reaction rate, then for two reacting substances A and B, the rate equation assumes the form:

$$r = \frac{kK_AK_B[A][B]}{(1 + K_A[A] + K_B[B])^2} \qquad (4)$$

where k is the surface reaction rate constant and K is the adsorption equilibrium constant.

Table 1
Determined reaction rate constants of singlet oxygen with 2-CP and RB

Rate constant ($dm^3\,mol\,s$)	This work		[19]		[20]	[15]	
	2-CP	2-CP anion	2-CP	2-CP anion	2-CP anion	2-CP	2-CP anion
k_r	$(1.5 \pm 0.1) \times 10^5$	$(8.1 \pm 0.7) \times 10^7$	$\sim 9 \times 10^6$	1.9×10^8	2.2×10^8	3.8×10^5	–
$k_Q^{2\text{-CP}}$	$(7.0 \pm 1.8) \times 10^7$	$(9.5 \pm 3.7) \times 10^8$				4.8×10^7	7.26×10^8
k_t	$(1.3 \pm 3.6) \times 10^6$	$(1.2 \pm 0.5) \times 10^9$			6.8×10^8	1.3×10^6	2.36×10^9

If we assume that both substrates adsorb in separate places, i.e., they do not compete for active centers on the surface, the rate equation has the form:

$$r = \frac{kK_A K_B [A][B]}{(1 + K_A[A])(1 + K_B[B])} \tag{5}$$

When product $K_A[A]$ is less than unity, the constant has a small value and substrate concentration is low and the rate equation simplifies to the form resulting from the so-called Langmuir–Rideal mechanism [21]:

$$r = \frac{kK_A K_B [A][B]}{1 + K_B[B]} \tag{6}$$

Basing on the results in the homogeneous system, we assume that the 2-CP degradation in the heterogeneous system occurs mainly in the reaction with $^1O_2$ as well.

In further considerations, it should be determined whether the reaction takes place on the surface only. The adsorbed oxygen after having reacted with the photosensitizer gives $^1O_2$ which can pass on the surface to meet 2-CP, or can desorb and react with 2-CP in the solution. The lifetime of $^1O_2$ in the aqueous solution is long enough (4 μs [22]) to make us consider such an alternative.

The next problem is the competitiveness of oxygen and 2-CP adsorption. Except for the reaction substrates, water and inorganic particles, as buffer components, can adsorb on the gel surface as well. These processes can limit the accessible surface causing a decrease of the degradation rate. Essential from the point of view of $^1O_2$ formation is the adsorption of oxygen in places of the photosensitizer immobilization. The lifetime of excited RB is about 150 μs [2], and in the gel, it is probably extended, which should not hinder the diffusion of oxygen from quite distant places on the surface. Hence, it can be supposed that 2-CP and oxygen can be adsorbed in the same active centers. Only the chemical nature of additional gel components may cause that on the surface there will be such places where adsorption of one of the substrates is privileged.

Results of our experiments [14] with 2-CP degradation using the gel with embedded RB as a photosensitizer show that the reaction rate is directly proportional to oxygen concentration and it depends to a certain extent also on 2-CP concentration. In the lower range of 2-CP concentration the reaction rate increased, but at higher substrate concentrations the rate stabilized and remained constant, which is shown on the plot in Fig. 4 (for pH 6). It indicates that the photosensitized reaction proceeded on the gel surface and high 2-CP content caused saturation of active sites on the gel.

The experimental results were used to verify theoretical dependences of the reaction rate on 2-CP concentration (Fig. 4). Eq. (4), in which competition of oxygen and 2-CP for active centers on the gel was assumed, did not provide a correct description of the dependence.

Good results were obtained for Eq. (6), which can indicate that there are places on the gel surface with different adsorption preferences. For Eq. (6), the curve fitting is much better than in other cases, so the determined parameters are more reliable, but
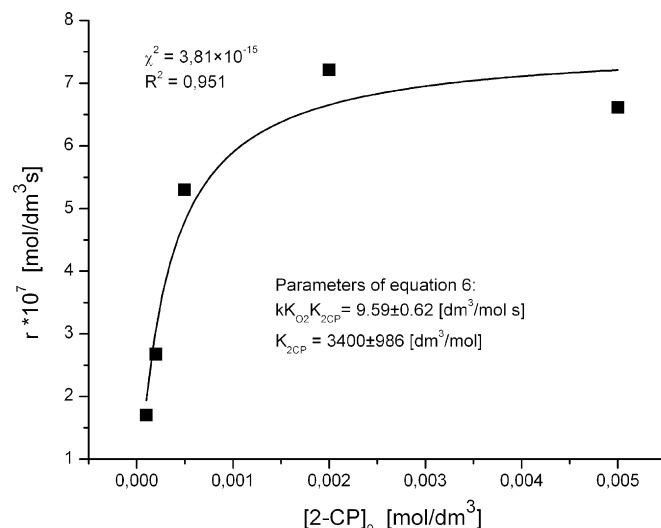

Fig. 4. Dependences of the initial reaction rate at pH 6 on initial 2-CP concentration in the heterogeneous system with RB as a sensitizer, lines are the theoretical course according to Eq. (5), points are the experimental results.

still burdened with a considerable error. However, these are only the parameters of an experimental equation.

In order to assign the character of physical values to the kinetic parameters determined on the basis of L–H kinetics, additional preliminary experiments were made aiming at determination of the parameters of oxygen and 2-CP adsorption on silica gel.

3.2.1. The examination of oxygen adsorption on silane gel

It was difficult to determine in a classical way the parameters of oxygen adsorption from an aqueous solution on silica gel. Hence, an attempt was made to carry out the investigation using the process of RB fluorescence quenching by molecular oxygen [23]. From the point of view of the research of singlet oxygen being formed due to the contact of dye sensitizer with oxygen, this method for the determination of adsorption constants seems very adequate.

If the gel is in contact with deoxygenated aqueous solution, then the emission of immobilized dye (I_0^f) is proportional to the quantity of RB distributed on the whole surface. When the solution is aerated to a definite concentration, the measured fluorescence (I^f) will be lower as a result of quenching the excited singlet state of the photosensitizer. Processes of fluorescence quenching are described by the Stern–Volmer relationship:

$$\frac{I_0^f}{I^f} = 1 + K_{SV}[\theta] \tag{7}$$

where K_{SV} is the Stern–Volmer constant; θ, is the fraction of a surface covered by adsorbed molecules.

According to the Langmuir isotherm, θ is represented by the following equation:

$$\theta = \frac{K_{O_2}[O_2]}{1 + K_{O_2}[O_2]} \tag{8}$$

The substitution of Eqs. (8) and (7) gives:

$$\frac{I_0^f - I^f}{I^f} = \frac{K_{SV}K_{O_2}[O_2]}{1 + K_{O_2}[O_2]} \tag{9}$$

Experiments were carried out in spectrophotometric cuvettes with plates coated with gel containing RB. Water was poured into the cuvettes and nitrogen, air, 50/50 (vol.) nitrogen and oxygen mixture and pure oxygen were introduced. Next, the plates were inserted and fluorescence was measured at the excitation of the photosensitizer with the wavelength 648 nm. Results of the measurements calculated according to Eq. (9) are presented graphically in Fig. 5. They were used to determine adsorption equilibrium constants for the silane gel–oxygen system.

3.2.2. The examination of 2-chlorophenol adsorption on silane gel

The 2-CP adsorption was analyzed typically by determination of equilibrium concentration using the chromatographic method. The aqueous solution of 2-CP with a defined concentration was introduced to the plate reactor with gel-covered walls, which ensured the process proceeded in the dark. The inner surfaces of glass plates were covered with gel containing the immobilized dye sensitizer. The quantity of adsorbed 2-CP was determined from the difference of initial concentration and after reaching equilibrium in the aqueous solution. The series of experiments carried out for different initial 2-CP concentrations allowed us to draw adsorption isotherm (Fig. 6).

The character of the curve is different from that of a typical Langmuir isotherm, it reminds a BET-type adsorption curve. This may suggest that at high concentrations of 2-CP, the organic phase is separated on the gel surface. However, for initial run of the curve, the adsorption equilibrium constant was determined according to the Langmuir equation (Eq. (10)), because the experiments with 2-CP degradation were not performed at such high concentrations.

$$[2\text{-CP}]_{ad} = \frac{[2\text{-CP}]_{max}K_{2\text{-CP}}[2\text{-CP}]}{1 + K_{2\text{-CP}}[2\text{-CP}]} \tag{10}$$
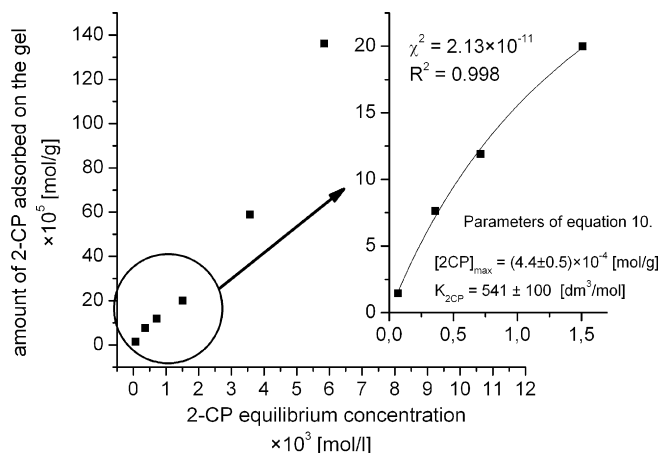
Fig. 6. The isotherm of 2-CP adsorption on silica gel. Inset: estimation of adsorption parameters according to the Langmuir equation.

The knowledge of the values of equilibrium constants K_{O_2} and $K_{2\text{-CP}}$ allowed us to calculate surface rate constants of 2-CP degradation in the heterogeneous system. According to Eq. (6), the value of k equals to 1.63×10^{-4} mol dm^{-3} s^{-1}.

Further investigations of the heterogeneous system like equilibria and kinetic studies of substrates and water adsorption on the gel are necessary to explain the positive effect of immobilization.

4. Conclusions

In this paper the decomposition of 2-CP in an aqueous solution by means of photosensitized oxidation using RB was studied. Chlorophenols have become of environmental concern due to their acute toxicity and resistance to biodegradation. The described method is especially attractive because of the possibility of using oxygen from air and solar photons in visible range. In the homogeneous system the established kinetic model allowed us to determine rate constants of the chemical and physical reaction of singlet oxygen with 2-CP and the rate constant of physical quenching excited triplet RB by 2-CP.

The silane gel based on TEOS is proved to be a useful water nonsoluble carrier for immobilization of a sensitizer. The results of experiments allowed us to estimate the kinetic parameters. The L–H type mechanism was used to describe the process. In order to assign the character of physical values to the L–H kinetic parameters, an attempt was made to determine the Langmuir parameters of oxygen and 2-CP adsorption on silica gel.

The good understanding and explanation of processes undergoing in the heterogeneous system require further investigation.

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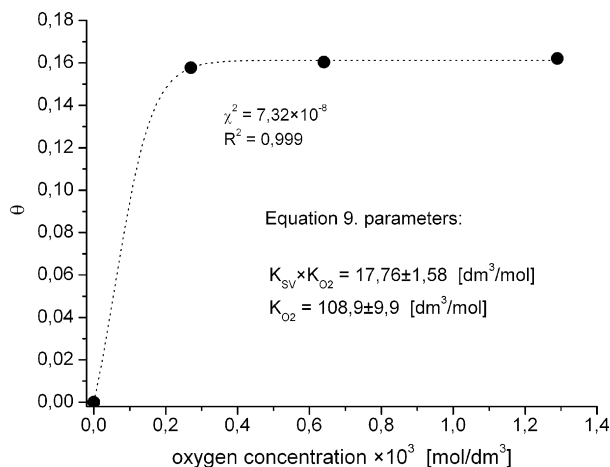
Fig. 5. The Langmuir relation determined from the measurements of rose bengal fluorescence quenching with oxygen (points). Line represents the curve based on Eq. (8).

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