



Determination of the photocatalytic deposition velocity



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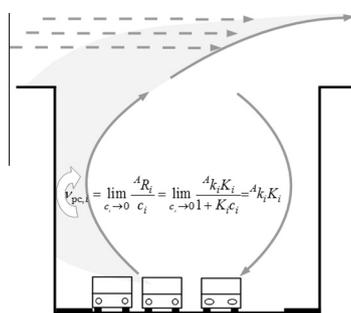
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HIGHLIGHTS

- A definition of the photocatalytic deposition velocity is given.
- Photocatalytic deposition velocities of NO and NO₂ are calculated.
- A photoreactor as described in ISO 22197-1 was used.

GRAPHICAL ABSTRACT



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ABSTRACT

Microscale atmospheric dispersion models have been employed recently to predict the possible effect of photocatalytically active surfaces on the air pollution in urban areas. These simulations use the photocatalytic deposition velocity as an input value. However, no generally accepted experimental method for the determination of the photocatalytic deposition velocity is available. Here a method to determine the photocatalytic deposition velocity is proposed which is based on ISO 22179-1 *et seqq.* specifying test methods for the determination of the air-purification performance of materials that contain a photocatalyst or have photocatalytic films on the surface. It is assumed that the rate of the photocatalytic surface reaction of a species i , A_{R_i} , is given by an expression having the mathematical form $A_{R_i} = A_{k_i} K_i c_i / (1 + K_i c_i)$ where the kinetic parameters A_{k_i} and K_i are variables depending on the photon flux, the temperature, the humidity and the concentration of other pollutants. Under steady state conditions the mole balance of a differential volume of a fluid element inside the plug flow reactor described in the cited ISO standards reads $Y = A_{k_i} K_i X - \text{const}(i)$. This equation is a linear equation of the two variables $Y = \ln(c_{in,i}/c_{out,i}) / (c_{in,i} - c_{out,i})$ and $X = A_r / (q_v(c_{in,i} - c_{out,i}))$ where $c_{in,i}$, $c_{out,i}$, A_r , and q_v are the inlet and outlet concentration of the pollutant i under consideration, the irradiated photocatalytically active surface, and the volumetric flow rate through the photocatalytic reactor, respectively. It is argued that the slope $A_{k_i} K_i$ of this equation is the demanded photocatalytic deposition velocity $v_{pc,i}$. Thus, the measurement of $c_{out,i}$ at varying $c_{in,i}$ makes the photocatalytic deposition velocity accessible.

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1. Introduction

The potential impact of proposed measures for air pollution control in urban areas is commonly simulated using microscale atmospheric dispersion models [1]. The mathematical simulation how air pollutants disperse in the ambient atmosphere is

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Nomenclature

A_c	cross sectional area of a plug flow reactor (m^2)	A_R	rate of a chemical reaction per unit surface area ($mol\ m^2\ s^{-1}$)
A_r	photocatalytically active (geometric) surface area (m^2)	V_R	rate of a chemical reaction per unit volume ($mol\ m^3\ s^{-1}$)
c	concentration ($mol\ m^{-3}$ or ppm_v)	t	time (s)
E	irradiance or molar photon flux ($W\ m^{-2}$ or $mol\ photons\ m^{-2}\ s^{-1}$)	V_r	volume of photoreactor or volume of fluid over a photocatalytically active sample (m^3)
F	deposition flux on a surface ($mol\ m^{-2}\ s^{-1}$ or $ppm_v\ m^{-2}\ s^{-1}$)	W	width of photoreactor or width of photocatalytically active sample (m)
h_a	absolute humidity ($g\ m^{-3}$)	λ	wavelength (m)
h_r	relative humidity (%)	v_d	deposition velocity ($m\ s^{-1}$)
H	height over the photocatalytically active sample inside the photoreactor (m)	v_{pc}	photocatalytic deposition velocity ($m\ s^{-1}$)
A_k	kinetic parameter of a surface reaction ($mol\ m^2\ s^{-1}$)	ϑ	temperature ($^{\circ}C$)
k_a	kinetic parameter ($m\ s^{-1}$)	<i>Subscripts</i>	
k_d	kinetic parameter ($mol\ m^{-2}\ s^{-1}$)	i	chemical species under consideration
$k_r\eta$	kinetic parameter of a surface reaction ($mol\ m^2\ s^{-1}$)	in	inlet conditions
K	kinetic parameter ($m^3\ mol^{-1}$)	out	outlet conditions
L	length of photocatalytically active sample (m)		
q_v	volumetric flow rate of fluid ($m^3\ s^{-1}$)		
r_a, r_b, r_s, r_r	aerodynamic resistance, sub-layer resistance, surface resistance, and resistance of chemical reaction ($s\ m^{-1}$)		

performed with computer programs that solve the mathematical equations which describe the pollutant transport in the gas phase and the interaction with surfaces. Recently, prognostic atmospheric dispersion models such as MIMO [2,3], ENVI-met [4], MISKAM [5,6], and LASAT [7] have been used to predict the possible effect of photocatalytically active surfaces on the air pollution in urban areas. These simulations are calculating the dry deposition flux F_i of a pollutant i onto a surface. A flux F is generally defined as $(resistance)^{-1} \cdot (driving\ force)$ [8]. Accordingly, in the atmospheric dispersion models used to model the distribution of pollutants in an urban environment, the dry deposition flux F_i of the pollutant i onto a surface is defined as

$$F_i = \frac{1}{r} c_i \quad (1)$$

where r and c_i being the total resistance, which is the sum of individual resistance terms for each zone the pollutant has to cross on its way to the surface, and the concentration in the free atmosphere (or at a reference height over the surface) of the species i under consideration, respectively [5,9–11]. The reciprocal of the total resistance r is termed the deposition velocity $v_{d,i}$. Eq. (1) can be rewritten as

$$F_i = v_{d,i} c_i \quad (2)$$

giving the definition of the deposition velocity [12]. It has to be emphasized that the commonly used atmospheric dispersion models require a concentration-independent deposition velocity as an input parameter. Photocatalytically active surfaces are incorporated into these models by inserting an additional resistance term being the inverse of a photocatalytic deposition velocity $v_{pc,i}$. Values of the photocatalytic deposition velocity of nitrogen oxides have been determined using different experimental set-ups as well as different methods of data evaluation. Maggos et al. used a $30\ m^3$ environmental chamber as a batch reactor and analyzed the change of concentration of NO and NO₂ to calculate the photocatalytic deposition velocity with

$$v_{pc,i} = \frac{2V_r(c_{0,i} - c_{t,i})}{A_r t(c_{0,i} + c_{t,i})} \quad (3)$$

where $(c_{0,i} + c_{t,i})/2$ is the average concentration inside the photoreactor [13]. Maggos and co-workers also employed a $917\ m^3$ continuous-flow photocatalytic reactor for the photocatalytic oxidation of NO, NO₂, and other compounds in automobile exhaust gas. In this case

$$v_{pc,i} = \frac{2q_v(c_{in,i} - c_{out,i})}{A_r(c_{in,i} + c_{out,i})} \quad (4)$$

was used to calculate the photocatalytic deposition velocities [14]. The same equation was used by Kontos et al. who investigated the NO oxidation at nanotubular TiO₂ films ($10.7 \cdot 10^{-4}\ m^2$) in a continuous-flow reactor ($0.001\ m^3$). They observed an inverse dependence of $v_{pc,NO}$ on both the initial concentration and the volumetric flow rate [15]. Flassak et al. have determined the photocatalytic deposition velocity of NO and NO₂ in ambient air on a paint sample ($1.24\ m^2$) in a flow-through reactor ($0.185\ m^3$). Assuming first-order kinetics they derived

$$v_{exp} = \frac{q_v}{A_r} \ln \left(\frac{c_{in,i}}{c_{out,i}} \right) \quad (5)$$

which was corrected to get photocatalytic deposition velocities unaltered by mass transport limitations [5]. Bruse and Droll have used a continuous stirred tank photoreactor with a volume of $2.5 \cdot 10^{-3}\ m^3$ to investigate the photocatalytic NO oxidation on concrete surfaces ($50 \cdot 10^{-4}\ m^2$). They have calculated the photocatalytic deposition velocity without giving details.[4]

As becomes obvious from this compilation, till this day the photocatalytic deposition velocity has not been defined unequivocally, and no generally accepted experimental method for the determination of the photocatalytic deposition velocity is available.

Here, the photocatalytic deposition velocity is defined, and a method to determine the photocatalytic deposition velocity is proposed which is based on ISO 22179-1 *et seqq.* specifying test methods for the determination of the air-purification performance of materials that contain a photocatalyst or have photocatalytic films on the surface. The behavior of the photocatalytic reactor stipulated in these standards for the analysis of non-porous samples is approximated using a plug flow reactor as the reactor model.

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