The Effect of Various Process Conditions on the Photocatalytic Degradation of NO

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Abstract. This paper presents the research conducted on photocatalytic concrete products with respect to the evaluation of the effect of varying process conditions on the degradation of nitric oxide (NO). The degradation process under laboratory conditions is modeled using the Langmuir-Hinshelwood kinetic model as basic reaction model. The suitability of the model is validated by experimental data as well as data obtained from literature. Furthermore, the effect of variations of process conditions like irradiance and relative humidity on the reaction rate constant k and adsorption equilibrium constant K_d are considered in the model.

1 Introduction

Air-quality in inner city areas is a topic which already receives a lot of attention nowadays. But in the coming years, the overall interest in this special topic will be bigger as there will be a number of conflicts with the limiting values given by the European Council [1]. These conflicts are caused on the one hand by a reduction of already existing limiting values till 2010 and increasing traffic rates, especially for diesel powered passenger cars and freight vehicles, on the other hand.

A promising approach for solving the problem of nitrogen oxides (NO_x) is the photochemical conversion of nitrogen oxides to low-dosed nitrates due to heterogeneous photocatalytic oxidation (PCO). The reaction products in form of nitrate compounds are water soluble and will be flushed from the active concrete surface by rain. The nitrate compounds can subsequently be extracted from the rain water by a standard sewage plant. For the photocatalytic oxidation, titanium dioxide (TiO_2) in low concentration is applied as photocatalyst. This photocatalyst uses light in the UV-A range of the sun light for the chemical conversion of nitrogen oxides.

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The basic working principle of the photocatalytic process is well know and discussed manifold in literature [2, 3]. First efforts in large scale applications of the photocatalytic reaction for air-purifying purposes have been made for about 10 years in Japan and have been also adopted by the European market [4]. But these investigations, as well as the fundamental research, are limited to single products only. A comparative study on the NO_x degradation of active concrete surfaces is discussed in [5]. The present paper is a continuation of this research using the results derived with one of the evaluated paving blocks as basis for further analysis. The basic principle of the test setup used as well as the conduction of the measurements are discussed in [6] and oriented on [7].

A reaction model is derived by using varying volumetric flow scenarios as well as different pollutant concentrations while the remaining test conditions have been kept constant. The reaction model describes the sample in terms of a reaction rate constant k and an adsorption equilibrium constant K_d. As changes of the relative humidity and UV-A irradiance can considerably change the efficiency of the PCO, their influence on the reaction is investigated and described by the model.

2 Reaction Model

The PCO at the surface of the paving block can be considered as heterogeneous catalysis [2] and is therefore characterized by adsorption of the pollutant molecules and desorption of the reaction products. It is demonstrated in [8] that not the diffusion but the conversion is the rate limiting step. For the prevailing photocatalytic gas-solid reaction, only adsorbed NO can be oxidized. Therefore, the Langmuir-Hinshelwood rate model is used for the modeling as suggested by [3, 9] and will also be applied here. According to the model, the disappearance rate of reactants reads:

$$r_{NO} = \frac{kK_d C_g}{1 + K_d C_g} \tag{1}$$

with k as reaction rate constant (mg/m^{3}s), K_d as the adsorption equilibrium constant (m^3/mg) and C_g as the NO concentration (mg NO per m^3 air) in the inlet gas. The NO balance equation now reads:

$$v_{air} \frac{dC_g}{dx} = -r_{NO} = -\frac{kK_d C_g}{1 + K_d C_g} \tag{2}$$

Supposing that $C_g = C_{g,in}$ and considering the reactor geometry, integration of Eq. (2) yields:

$$\frac{1}{k} + \frac{1}{kK_d} \frac{Ln\dfrac{C_{g,in}}{C_{g,out}}}{(C_{g,in} - C_{g,out})} = \frac{L}{v_{air}(C_{g,in} - C_{g,out})} = \frac{V_{\mathrm{Re}actor}}{Q(C_{g,in} - C_{g,out})} \tag{3}$$

as $V_{Reactor} = LBh$ and $Q = v_{air}Bh$, again, $C_{g,out} = C_g(x = L)$. In Table 1 the values for $C_{g,out}$ for the experiments with one paving block are summarized. The inlet concentration $C_{g,in}$ was adjusted to 0.1, 0.3, 0.5 and 1 ppm NO (equivalent to 0.135, 0.404, 0.674 and 1.347 mg/m^3) and the flow rate Q was 1, 3 and 5 l/min.

Table 1 NO outlet concentrations of the reactor considering varying inlet concentrations and flow rates for the photocatalysis of the paving block example

$C_{g,in}$	$C_{g,out}$ [ppm]			NO_x removal rate [%]		
[ppm]	Volumetric flow rate Q [l/min]			Volumetric flow rate Q [l/min]		
	1	3	5	1	3	5
0.1	0.011	0.032	0.041	89.0	68.4	59.4
0.3	0.039	0.157	0.197	87.1	47.6	34.3
0.5	0.210	0.309	0.356	58.0	38.3	28.9
1.0	0.334	0.729	0.779	66.6	27.1	22.1

In Figure 1a, $y = V_{Reactor}/Q(C_{g,in}-C_{g,out})$ is set out versus $x = Ln(C_{g,in}/C_{g,out})/(C_{g,in}-C_{g,out})$ and the data fit with the line $y = 1.19x+2.37$ obtained by the regression analysis. The intersection with the ordinate corresponds to $1/k$ so that k = 0.42 mg/m^{3}s and the slope of the regression line is corresponding to $1/kK_d$ so that K_d = 2.00 m^3/mg. By means of the obtained values of k and K_d the conversion rate and diffusion rate can be compared (cp. [8]).

Further relevant data on photocatalytic reactions could be found in [10]. Here, the paving block type NOXER was exposed to varying NO concentrations. With the help of background information regarding the conduction of the measurement, the Langmuir-Hinshelwood model could be applied. Using the data given in [10], a linear fit was derived as given in Figure 1b. The given data result in k = 3.54 mg/m^{3}s and K_d = 0.538 m^3/mg. Compared with own experiments, the conversion

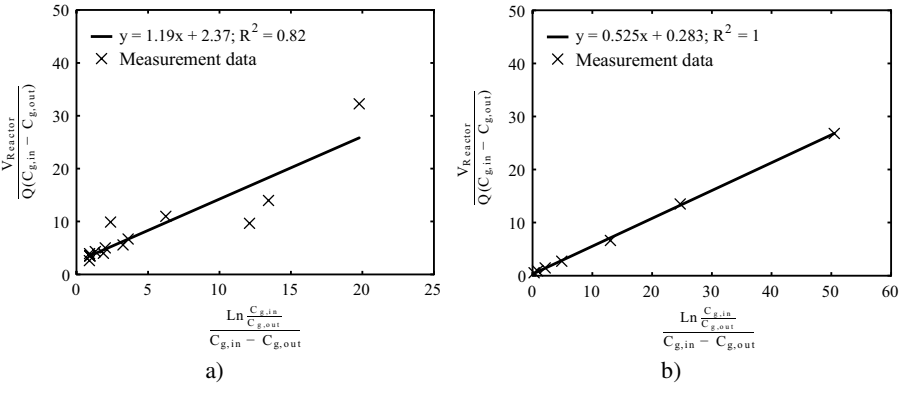


Fig. 1 Regression results of experimental data. a) own measurements presented in Table 1. b) data taken from [10]

rate is notedly higher and relatively less smaller than the diffusion transfer rate. This can be explained for the conversion by varying amounts and types of TiO_2 whereas the diffusion could be influenced by different surface morphology of the paving blocks. However, the data given in [10] are in good agreement with the model.

3 Modeling of External Influences

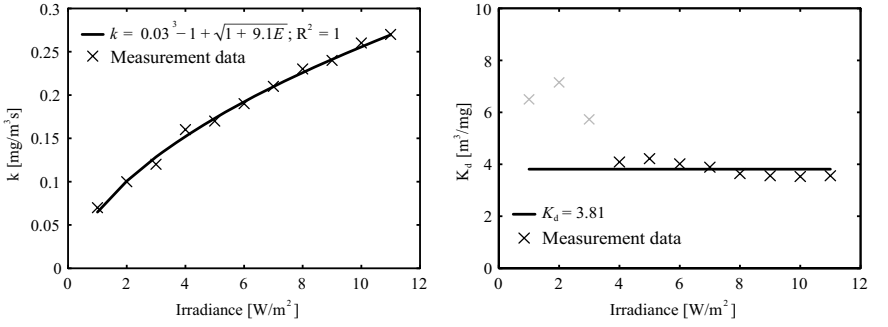
The degradation of NO and therewith the performance of the photocatalytic reaction is governed by physicochemical as well as product related parameters. In the previous section, a general model for the reaction kinetics has been derived considering reaction kinetics and flow related parameters. However, for a comprehensive modeling two further external influencing factors of the degradation process have to be considered. These are the UV-A irradiance and the concentration of water, expressed by the relative humidity.

To start the photocatalytic degradation process, UV-A light of the appropriate wavelength λ and irradiance E is necessary. According to [2], the increasing photocatalytic activity caused by increased irradiance can be divided into two regimes: i) for $E \leq 250$ W/m^2 the degradation increases proportional to E and ii) for $E > 250$ W/m^2 the photocatalytic activity grows as the square root of E. This linear behavior in the range of low irradiance ($E < 15$ W/m^2) could not be confirmed be own experiments [11]. In order to incorporate the dependency of the reaction constant k on the UV-A irradiance, a suitable mathematical expression can be found in [12]. Therewith, the reaction rate constant k would read:

$$k = \alpha_1\left(-1+\sqrt{1+\alpha_2 E}\right) \tag{4}$$

With α_1 and α_2 being factors to be fitted from the experiment. The expression considers the linear and nonlinear behavior of the degradation process for varying UV-A irradiance. The experimental data as well as the fit of Eq. (4) are depicted in Figure 2a and show good agreement. It is assumed that the adsorption equilibrium constant K_a is not influenced by the UV-A irradiance. This assumption is also confirmed by the experimental data in Figure 2b. The grey marked values in Figure 2b are considered as outliers due to remarkable scattering in the measurement caused by low flow values combined with low inlet pollution.

The influence of the relative humidity RH is caused by the hydrophilic effect of TiO_2 under exposure to UV-A light. According to [4], the hydrophilic effect at the surface is gaining over the oxidizing effect when high relative humidity values are applied. The water molecules adsorbed at the surface prevent the pollutants to react with the TiO_2. Therefore, it is assumed that both the conversion of NO and the adsorption of NO at the surface is affected. Considering the experimental data



a) b)

Fig. 2 Influence of UV-A irradiance. a) reaction rate constant *k*. b) adsorption equilibrium constant K_d.

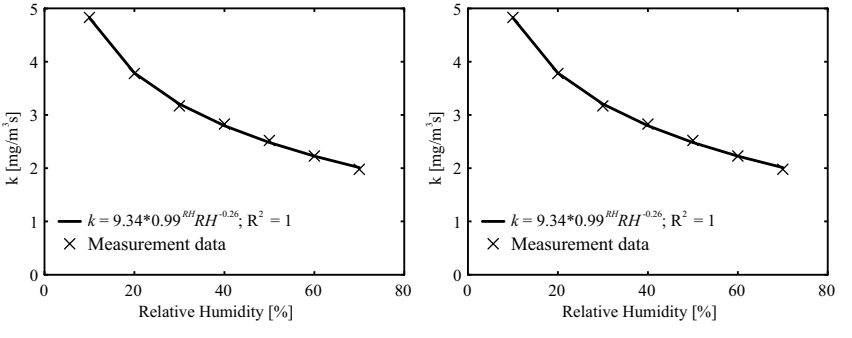
given in Figure 3a and 3b, the influence of the relative humidity on the reaction rate constant *k* can be explained by:

$$k = \alpha_3 \alpha_4^{RH} RH^{\alpha_5} \tag{5}$$

while the dependency of the adsorption equilibrium constant K_d is expressed by a quadratic function:

$$K_d = \alpha_6 RH^2 + \alpha_7 RH + \alpha_8 \tag{6}$$

The fitting of the parameters α_3 to α_8 showed a good agreement with the experimental data (cp. Figure 3a and 3b).



a) b)

Fig. 3 Influence of relative humidity. a) reaction rate constant *k*. b) adsorption equilibrium constant K_d.

4 Conclusions

The heterogeneous photocatalytic oxidation seems to be a promising technique for reducing air pollution in inner city areas with high emissions of nitrogen oxides caused by increasing traffic loads. Numerous measurements of this research project carried out within the last two years showed that the concentration of nitrogen oxides in the ambient air can be effectively reduced by the photocatalytic oxidation using TiO_2. The experimental data provide a basis for the modeling of the degradation process using the Langmuir-Hinshelwood kinetics. The prediction of the performance of certain air-purifying concrete products can now be predicted by the derived model. Furthermore, mathematical expressions are proposed describing both the kinetic boundary conditions as well as the process conditions. The latter influences and the transformation of the results to practical applications is part of ongoing research.

Acknowledgments. The authors wish to express their thanks to the following sponsors of the research group: Bouwdienst Rijkswaterstaat, Rokramix, Betoncentrale Twenthe, Graniet-Import Benelux, Kijlstra Beton, Struyk Verwo Groep, Hülskens, Insulinde, Dusseldorp Groep, Eerland Recycling, ENCI, Provincie Overijssel, Rijkswaterstaat Directie Zeeland, A&G maasvlakte, BTE, Alvon Bouwsystemen, and v. d. Bosch Beton (chronological order of joining).

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