Photocatalytic degradation of air pollutants — From modeling to large scale application

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A B S T R A C T

Indoor as well as outdoor air quality and their limiting values remain a major problem to our present-day society. This paper addresses the modeling of the decomposition process of nitrogen monoxide (NO) on reactive concrete surfaces under the controlled exposition of a UV source. Within this model the external mass transfer of the pollutant and the internal molecule diffusion-reaction were considered. A first-order kinetics equation is derived with respect to the NO concentration and a site-competitive adsorption between NO/NO2 and water molecules, resulting in a dependence of the reaction kinetics on the relative humidity. Using the proposed model, a reaction rate constant k and an adsorption equilibrium constant Kd can be derived which describe an active paving stone accurately. Experimental results from a self-developed photoreactor with continuous flow mode were used to validate the proposed kinetic expression. Furthermore, the effect of variations in process conditions such as irradiance and relative humidity on the two constants k and Kd is investigated. All modeling work provides a sound foundation for the translation of this process to real outside conditions. In this regard an upcoming project in a Dutch city is described in brief.

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1. Introduction

In order to overcome atmospheric pollution problems, a number of removal techniques are available. Mostly these are filter systems taking the respective pollutant from the gaseous phase and transforming it into another state which is stored and accumulated. This actually is only a shift of the problem. Since about 10 years, however, literature increasingly reports about a process, the so-called photocatalytic oxidation (PCO), using a solid semiconductor catalyst activated by UV-radiation. These systems are already available in active filter devices and their reaction kinetics on certain pollutants is sufficiently described. Therefore, such tailor-made reactor systems can be applied to systematically improve local problems such as in office buildings or along production sites.

However, there is no large-scaled solution for outdoor application such as in highly frequented inner city areas yet. Therefore the use of photocatalytically active concrete paving blocks appears to be one of the most serious attempts to control air quality in terms of e.g. nitrogen oxide (NOx) contamination in congested urban areas. Although these concrete products are already commercially available, hardly anything concerning their reaction kinetics has been published yet.

PCO has now been applied to construction materials for more than a decade. The general mode of action of photocatalysis itself is already known since a much longer time. However, since Honda and Fujishima introduced the water decomposition phenomenon (Honda–Fujishima Effect) of a photoelectrochemical cell using a titanium oxide photo electrode, photocatalysts have attracted extensive interest [1]. Waste-water treatment especially in regard to pharmaceutical and diagnostic media residues [2] but also the treatment of waste water from dyeing factories [3] set a new motivation for further research. In construction industry the window pane was probably the first product coming on the market equipped with photocatalytic properties. But now also cementitious binders are combined with titanium dioxide in order to attach them with air-purifying and self-cleaning effects. The last mentioned feature actually was the original intention whereas the former was rather a side effect, discovered later.

In the air-purifying sense this chemical process is particularly effective when large connected surface areas (horizontal or vertical), preferably as close as possible to the pollutant source are equipped with photocatalytically active materials. Examples of pollutants which can be eliminated are numerous. It can be said that all natural organic matter (NOM), including hardly oxidizable organic compounds, volatile organic compounds (VOCs) such as benzene, aldehydes and toluene, and a variety of inorganic compounds such as NOx, SOx and NH3 can be oxidized. This paper will focus on the degradation performance of NO and more specifically on its
modeling. Nitrogen oxides are besides carbon dioxide, sulfur dioxide, gaseous ammonia, ozone and particulate matter the most critical pollutants of the present air quality. Furthermore, NO can be handled with ease in the lab and its detection and analysis does not require very complex test facilities.

Because of the preferred large-scale application mentioned above, the concrete paving stone has become one of the most recognized construction elements providing photocatalytic properties so far. These active paving stones are commercially available for a fairly long time. Their market launch was, first in Japan, at the end of the 1990th. Since then their efficiency was analyzed in several scientific papers. In [4] a comparative study was presented, analyzing a representative share of the active paving stones available from the European market. Furthermore, a measuring procedure was proposed allowing for device independent and comparative test results. The major conclusion of this investigation was that independent and comparative control is essential to evaluate the broad variety of available products which again show a wide range in efficiency.

A next major step in understanding and deeper analyzing PCO is the modeling of its reaction kinetics, which actually is the focus of this paper. Here the literature provides a large number of papers dealing with the reaction kinetics of the photocatalytic oxidation of VOCs in specially designed gas reactors, [5] for example describes the degradation of formaldehyde which is a typical indoor VOC, extensively existing in modern building materials and household products. The degradation of Trichloroethylene (TCE), an often used degreaser and solvent, was modeled by [6]. In [7], [8] and [9] the degradation of perchloroethylene (PCE), a substance similar to TCE but more critical due to its manifold decomposition products, is modeled. For a detailed discussion of the reaction pathways for photocatalytic oxidation of nitrogen monoxide to nitric acid (HNO₃) over TiO₂, the reader is referred to [17]. Here also the transient influence is investigated. This selection proofs that the modeling of PCO reaction kinetics is sufficiently accounted for in research. However, all mentioned papers refer to reactor setups which have been specifically designed for the purpose of treating polluted air. Most authors used the Langmuir–Hinselwood model to evaluate the photocatalytic degradation rate of the respective pollutants. To the authors’ knowledge, there are no papers addressing the reaction kinetics of active concrete paving stones yet. This is important for the understanding and optimization of these products, and therefore this will be developed in the present paper. Furthermore, also influencing factors such as relative humidity and irradiance level are incorporated in the presented model. Finally, a brief introduction will be given on an ongoing large-scale pilot project, where the lab based modeling experience is tried to be translated into real scale.

2. Experimental description

In order to perform modeling work, a constant and controlled test environment as well as a suitable sample needs to be available. As mentioned before, there are a number of photocatalytic concrete paving blocks available on the market. From a comparative study on active paving stones presented by [4] the stone with the highest efficiency was selected for further modeling experiments. It is believed that tests with highly reactive surfaces can reveal smaller deviations in the degradation rate, which would not become as obvious when testing samples with a generally lower degradation capability. The sample, an active paving block of the dimension 100 × 200 mm², is described in [4]. Here also the test setup, which was designed for tests on active paving stones, is described in more detail. The used reactor operates in steady state. It houses the paving stone in such a way that the polluted gas can only touch it along the reactive surface but due to the immediate diffusion of the reactant it can be modeled as a plug flow reactor. The flow of gas along the planar reaction surface is laminar and is conducted in a duct of variable height which is at the lower side limited by the paving stone surface and from above by a borosilicate glass pane. If not otherwise stated the slit height amounts to 3 mm. The Reynolds number of the flow reads:

\[ Re = \frac{\nu_{\text{air}} d_h \rho_{\text{air}}}{\mu_{\text{air}}} = \frac{2 \nu_{\text{air}} h \rho_{\text{air}}}{\mu_{\text{air}}} = \frac{2 Q}{B V_{\text{air}}} \]  

(1)

\( d_h \) is the hydraulic diameter of the considered channel, defined as four times the cross-sectional area divided by the perimeter. For the slit considered here, \( d_h = 2 \text{ h} \). Substituting \( Q = 31/\text{min}, B = 100 \text{ mm} \) and \( \nu_{\text{air}} = 1.51 \cdot 10^{-3} \text{ m}^2/\text{s} \) (1 bar, 20 °C) yields \( Re \approx 65 \). This low Reynolds number implies that the flow within the reactor cell is laminar. A fully developed parabolic velocity profile will be developed at \( L_a = 0.05 \text{ Re} \), where \( L_a \approx 20 \text{ mm} \) [10]. That means that only the first 10% of the slit length are influenced by entrance effects. In the remaining 90% of the reactor cell a fully developed laminar flow profile exists. Despite the laminar flow along only one reactive surface, the duct volume can be considered as a plug flow reactor. FEM models show that a concentration gradient will only develop in flow direction. The difference of the reactant along the height axis can be neglected due to the immediate diffusion. Experimental results underline this assumption.

A schematic diagram of the reactor cell is given in Fig. 1. The light intensity \( E \) is kept constant at 10 W/m² (300–400 nm). In Table 1 the applied process conditions are summarized.

3. Modeling

The following section refers to the modeling of the reaction kinetics. Parts of this section are already published in [11]. First, one should observe the general course of the multistage reaction. This reaction starts with the diffusion of NO at the concrete surface and continues with the conversion to NO₂. This means that the process contains two transfer steps, the mass transfer from gas to wall and the conversion at the active concrete surface. In line with findings by [12] and [13], it will be demonstrated that the conversion is the rate limiting step.

The NO mass flux from gas to adsorbing surface can be described by:

\[ i_{\text{h}} = \frac{ShD}{d_h} (C_g - C_w) = \frac{ShD}{2h} (C_g - C_w), \]

(2)

with \( d_h \), as hydraulic diameter, and \( C_g \) (mean mixed or bulk in gaseous phase) and \( C_w \) (on the surface) are the NO concentrations (in mg NO per m² air). The relation between \( C_g \) and \( C_{\text{con}} \) is as follows:

\[ C_g = \frac{M_{\text{NO}} \rho_{\text{air}}}{M_{\text{air}}} C_{\text{con}}. \]

(3)

Considering that the molecular mass of the deployed synthetic air (\( M_{\text{air}} \)) is 28.8 g/mole (80% \( M_{N_2} \) and 20% \( M_{O_2} \)), that of NO (\( M_{N_2} \)) is 30.0 g/mole, and that \( \rho_{\text{air}} \) is 1.204 kg/m³, it follows that \( C_g \) (in mg/m³)

Reactor cell (UV-A resistant)
Sealing compound
Glass plate (borosilicate glass)
Rubber seals
Paving block
Reactive surface (87 × 192 mm²)

Fig. 1. Schematic diagram of the reactor cell.
is about 1.254 \( C_{\text{m}} \) (in \( 10^{-6} \text{ mol/mol} = \text{ppmv} \)). These calculations are based on standard conditions which define \( T = 293.15 \) K and \( p = 101.325 \) kPa = 1 atm.

\( Sh \) from Eq. (2) refers to the Sherwood number, which in thermodynamics gives the ratio of convective to diffusive mass transport. For slits with one inert and one exchanging side, the side walls are neglected, \( Sh \) amounts to about 5 [14]. Furthermore, \( D \) the diffusion coefficient of NO in air can be estimated to be \( 1.51 \cdot 10^{-5} \text{ m}^2/\text{s} \), which is the kinematic viscosity of air (\( \nu_{\text{air}} \)).

### 3.1. Diffusion as limiting step

Now it is assumed that the diffusion of NO from the gaseous phase to the concrete surface is the limiting step. This implies a complete and instantaneous conversion which would turn the NO concentration at the surface to zero. The NO mass balance equation then reads:

\[
v_{\text{air}} \frac{dC}{dx} = -m = -\frac{ShD}{2h} C_{\text{g}},
\]

with as boundary condition:

\[
C_{\text{g}} = C_{\text{g,in}}.
\]

Integrating Eq. (4) and application of Eq. (5) yields:

\[
\frac{C_{\text{g,out}}}{C_{\text{g,in}}} = e^{-\frac{2hShD}{v_{\text{air}}}},
\]

with \( C_{\text{g,out}} = C_{\text{g}}(x = L) \) and \( L \) being the length of the active surface, which is 192 mm in this case. The variable \( h \) describes the height of the plug flow reactor volume, i.e. the slit height in this case (cp. Fig. 1). Substituting all variables, including \( v_{\text{air}} = 0.17 \) m/s and \( h = 3 \) mm, into Eq. (6) yields \( C_{\text{g,out}}/C_{\text{g,in}} \approx 0.007 \). In other words, in the case that the diffusion to the wall would be the rate limiting step, the exit concentration would be close to 1% of the inlet concentration, i.e. 99.3% of the NO would be converted. However, the present measurements and also previous research [4] learned this is not the case, so that the conversion rate at the surface cannot be ignored (cp. Tables 2 and 3).

### 3.2. Conversion as limiting step

In the following, it is now a priori assumed that the conversion is the rate limiting step, so that \( C_{\text{w}} \) now equals \( C_{\text{g}} \), which will be verified below.

For the prevailing photocatalytic gas–solid surface reaction, only adsorbed NO can be oxidized. In the past therefore the Langmuir–Hinshelwood rate model has been widely used, e.g. by [5,6,12,13,15] as well as [16], and will also be applied here. Following this model, the disappearance rate of reactant reads:

\[
r_{\text{NO}} = \frac{kK_C}{1 + K_C C_{\text{g}}},
\]

with \( k \) as reaction rate constant (\( \text{mg/m}^2\text{s} \)) and \( K_C \) as the adsorption equilibrium constant (\( \text{m}^3/\text{mg} \)). The NO balance equation now reads:

\[
v_{\text{air}} \frac{dC}{dx} = -r_{\text{NO}} = -\frac{kK_C}{1 + K_C C_{\text{g}}},
\]

Integration and using the boundary condition, Eq. (5), yields:

\[
1 + \frac{1}{K_C} \ln \left( \frac{C_{\text{g,in}}}{C_{\text{g,out}}} \right) = \frac{L}{v_{\text{air}}(C_{\text{g,in}} - C_{\text{g,out}})} = \frac{V_{\text{reactor}}}{Q(C_{\text{g,in}} - C_{\text{g,out}})},
\]

with \( V_{\text{reactor}} = LBh \) and \( Q = v_{\text{air}} Bh \), and again, \( C_{\text{g,out}} = C_{\text{g}}(x = L) \). In Table 2 this \( C_{\text{g,out}} \) of the experiments with the paving stone is summarized.

The inlet concentration \( C_{\text{g,in}} \) had values of 0.1, 0.3, 0.5 and 1 ppmv NO (or 0.125, 0.376, 0.627 and 1.254 mg/m\(^3\)), and the flow rate \( Q \) was 1, 3 and 5 l/min.

### 3.3. Validation of the model

In Fig. 2, \( y = V_{\text{reactor}}/(Q(C_{\text{g,in}} - C_{\text{g,out}})) \) is set out versus \( x = \ln(C_{\text{g,in}}/C_{\text{g,out}})/(C_{\text{g,in}} - C_{\text{g,out}}) \), and the data fit with the line \( y = (1.19 \pm 2.37 \text{ m}^3/\text{mg})x \). The intersection with the ordinate corresponds to 1/k, so that \( k = 0.42 \text{ mg/m}^2\text{s} \), and the slope to 1/k\( K_C \) so that \( K_C = 2.00 \text{ mg/m}^3 \).

Reviewing the relevant literature, to the knowledge of the authors, no such data on the photocatalysis of concrete can be found. In [16] obtained \( k = 6.84 \text{ mg/m}^3\text{s} \) and \( K_C = 1.13 \text{ m}^3/\text{mg} \) was gained for the NO degradation by woven glass fabrics, their NO inlet concentration being in the range 40–80 ppmv. Concerning the photocatalytic ammonia degradation by cotton woven fabrics, [13] obtained \( k = 0.10 \text{ mg/m}^3\text{s} \) and \( 0.24 \text{ mg/m}^3\text{s} \), and \( K_C = 0.035 \text{ mg/m}^3 \) and \( 0.112 \text{ m}^3/\text{mg} \), whereby the NH\(_3\) inlet concentration ranged from 14 to 64 mg/m\(^3\).

With an in principle similar reactor (one reactive surface but no packed bed) [17] obtained a \( K_C \) of about 1.1 m\(^3\)/mg, applying NO levels from 5 to 60 ppm. As can be seen from this brief literature review, the respective constants vary as expected but are located in the same order of magnitude. It is assumed that the photocatalytic oxidation of NO is exclusively promoted by TiO\(_2\), therefore the constants should be similar. However, the boundary conditions broadly vary and cannot be compared from experiment to experiment. Therefore, also the cross-check of literature values with each other does not lead to matches. The influence of the light spectrum, the type of TiO\(_2\),
the slit height should not in
trolled process with a high diffusion rate is indeed true, then a change in
executing experiments with varied slit heights of 2 and 4 mm, besides
external mass transfer is also not identi
[18] who found conversion rates proportionally increasing with the
catalytic acting concrete has not been analyzed so far.

Fig. 2. Regression results of data presented in Tables 2 and 3 for the photocatalysis of
the paving stone example.
surface roughness of the paving sample and the catalyst concentra-
tion, to only mention a few, is at this moment too complex to be fully
considered in a model to be developed.

With the obtained values of \( k \) and \( K_d \) the conversion rate and
diffusion rate can be compared. Dividing the conversion/transfer rates
as governed by Eqs. (8) and (4) yields \( kK_d \) and, substituting the
prevailing values reveals that this ratio is about 0.2, i.e. the diffusion
rate is about five times the conversion rate. Note that the employed
\( kK_d \) is an upper limit for \( kK_d/(1 + K_dC) \), so that the actual ratio will
even be smaller. From this small conversion/transfer rate ratio one can
conclude that indeed the degradation rate is much lower than the
diffusion rate, and hence it is the limiting rate. This is also confirmed by
[18] who found conversion rates proportionally increasing with the
specific surface area of the applied titanium dioxide. In [17] the
external mass transfer is also not identified to be the limiting step.

In the present research this fact was furthermore investigated by
executing experiments with varied slit heights of 2 and 4 mm, besides
the standard 3 mm. When the assumption of a mainly conversion con-
trolled process with a high diffusion rate is indeed true, then a change in
the slit height should not influence the degradation performance. \( C_{g,\text{in}} \)
was now taken as 0.376 mg/m³ (0.3 ppmv) and the flow rate \( Q \) was 1, 3
and 5 l/min. In Table 3, and also in Fig. 2, this data is included. Except
for the smallest flow rate (\( Q = 1 \) l/min), the degradation rates match
well with the values listed in Table 2, and the computed \( V_{\text{reactor}}/Q(C_{g,\text{in}} - \)
\( C_{g,\text{out}} \) and \( \ln(C_{g,\text{in}/C_{g,\text{out}}})/(C_{g,\text{in}} - C_{g,\text{out}}) \) are also compatible with the
previous ones set out in Fig. 2 and the fitted trend line.

The above literature review shows that the Langmuir–Hinshel-
wood model has been frequently applied to characterize photocata-
lytic gas–solid surface processes using various substrate materials. On
the other hand, to the authors’ knowledge, the kinetics of photo-
catalytic acting concrete has not been analyzed so far.

Other relevant data on photocatalysis on concrete was found in
[19]. Here, amongst other things, data is presented on the NOx removal
of a paving stone type (NOXER) which is exposed to varying NO
concentrations. With the help of background information regarding the
setup and conduction of measurement and analysis according to the
Langmuir–Hinshelwood model, similar to the one above, was
executed. The provided information about test setup and conditions
were sufficient for adequate application of the model. In order to allow
for a reproduction of the executed computations the boundary
conditions are briefly given in the following as being extracted from
[19]. The volumetric pollutant flow \( Q \) and the length of the sample
(reactor) \( L \) amount to 3 l/min and 200 mm, respectively. The slit
height \( h \) of the reactor was assumed to be 3 mm. As shown before, the
analysis is not sensitive to this measure anyway. The relative humidity
is given with 50% and the irradiance amounts to 6 W/m²

Using the data on the NOx removal rate given in Table 4, a linear fit
is derived as given in Fig. 3. It can be seen that the resulting data points
fit well into the proposed model. Note that here, in difference to Fig. 2,
only the NO concentration is varying but volumetric flow and slit
height are maintained the same.

Based on these values, again conversion rate and adsorption equilib
rium constant can be derived. For the given data, \( k \) amounts to
3.54 mg/m³/s and \( K_d \) to 0.538 m³/mg, respectively. Compared to the
previously discussed own experiments, the conversion rate constant is
notably higher and vice versa the adsorption equilibrium rate constant smaller. On the conversion side this can be explained with
different amounts and types of catalyst (anatase type) whereas the
diffusion could be influenced by different surface morphology of the
paving stones. The ratio of conversion/diffusion rates therefore
amounts to 0.457 for the NOXER case, though the conversion rate is
still more than twice the diffusion rate, it is less dominant now.

4. Extension of the model
In the former paragraph a general model for the reaction kinetics of heterogeneous photocatalytic oxidation on concrete substrates has
been derived. This model contains the reaction kinetics and flow
related parameters such as reactor dimension, volumetric flows and
pollutant concentration. The difficulty of predicting the performance
of a photocatalytic cementitious system including all pertinent factors
lies in the large number of variables involved. However, for a com-
prehensive modeling at least two more external influences on the
degradation efficiency have to be included into the model. These are
the irradiance and the water vapor concentration, expressed by the
relative humidity. Using these two influencing factors, the impact of
changing weather conditions can be accounted for by the model.

4.1. Irradiance

The degradation process of NO molecules is caused by the
photocatalytic activity of the catalyst surface. This photocatalytic
behavior results from the optoelectronic properties of the used
semiconductor. For the deployed catalyst (titanium dioxide in the
anatase modification), the UV-A light (\( \lambda \approx 380 \) nm) shows the most
suitable range regarding the wavelength \( \lambda \) to start the photocatalytic
oxidation. However, not only the wavelength is influencing the
efficiency of the system, but also the light intensity or irradiance \( E \)
has an effect on the degradation rate.

According to [20], the increase in the photocatalytic activity caused
by increased irradiance can be divided into two limiting cases: i) for
\( E \leq 250 \) W/m² the degradation increases proportional to \( E \) (linear
dependence) and ii) for \( E > 250 \) W/m² the photocatalytic activity grows with
the square root of \( E \) for high irradiance (square root
dependence). At very low range of irradiance (\( E < 10 \) W/m²),
where the present study needs to be placed, the dependency, however,
deviates from this linear relation.

<table>
<thead>
<tr>
<th>NO concentration [ppm]</th>
<th>NO removal [mmol/m²·12h]</th>
<th>NOx removal rate [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>0.2</td>
<td>89.0</td>
</tr>
<tr>
<td>0.1</td>
<td>0.4</td>
<td>88.9</td>
</tr>
<tr>
<td>0.2</td>
<td>0.8</td>
<td>90.6</td>
</tr>
<tr>
<td>0.5</td>
<td>2.0</td>
<td>88.4</td>
</tr>
<tr>
<td>1.0</td>
<td>3.7</td>
<td>82.3</td>
</tr>
<tr>
<td>2.0</td>
<td>6.1</td>
<td>68.0</td>
</tr>
<tr>
<td>5.0</td>
<td>10.0</td>
<td>44.3</td>
</tr>
</tbody>
</table>
K means every value of 0.1, 0.3, 0.5, 0.7 and 1.0 ppmv is conducted (11×5 matrix). That of measurements varying the NO inlet concentration in steps of again tends to α (the irradiance and the achieved values of k irradiance. The given function describes the relation between the determined in dependency of the respective irradiance level.

d is represented by a linear fit similar to the one presented in Fig. 2, which again is based on 5 individual measurements (55 data points). A summary of all line fits (y = mx + n), used for the further analysis, is given in Table 5. From these line fits reaction rate constants and adsorption equilibrium rate constants can be determined in dependency of the respective irradiance level.

Fig. 4 shows the dependence of reaction rate constant k on the irradiance. The given function describes the relation between the irradiance and the achieved values of k for low values of irradiance (E = 12 W/m²) adequately. The reaction rate constant k as a function of the irradiance E reads:

\[ k = \alpha_1 (-1 + \sqrt{1 + \alpha_2 E}) \],

with \( \alpha_1 \) and \( \alpha_2 \) being factors to be fitted from the experiment. This expression accounts for the linear and non-linear dependencies. When UV-radiation is absent, i.e. \( E = 0 \), the reaction rate becomes zero. For small E, Eq. (10) tends to become \( \alpha_1 \alpha_2 E/2 \), and for large E it tends to \( \alpha_1 \sqrt{\alpha_2 E} \). As can be seen from Fig. 4, \( \alpha_1 \) and \( \alpha_2 \) have been fitted for the considered active paving stone and amount to 0.03 mg/m³ and 9.1 m²/W, respectively. Fig. 4 illustrates that Eq. (10) is in good agreement with the experimental results.

The influence of varying irradiance on the adsorption equilibrium constant \( K_d \) is demonstrated in Fig. 5. Not taking the first three measurements for very low values of irradiance into account, the initial hypothesis that the irradiance has no influence on the adsorption behavior is confirmed. Here a constant \( K_d \) of 3.81 m³/mg can be derived for the respective paving stone sample. The first three outlying measurements represent very low irradiance levels where the light setup might not be stable enough. This concern is addressed in ongoing research. The disappearance rate of reactant from Eq. (7) hence is modified and now accounting for the influence of irradiance:

\[ r_{NO} = \frac{K_{d,NO} C_{NO}}{1 + K_{d,NO} C_{NO}} \alpha_1 (-1 + \sqrt{1 + \alpha_2 E}) \].

### 4.2. Relative humidity

The influence of the relative humidity depends to a large extent on the type of material used. According to [21], the hydrophilic effect at the surface is gaining over the oxidizing effect when high values of relative humidity are applied. The water molecules are adsorbed at

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**Table 5**

Summary of all line fits for the derivation of k and \( K_d \) in dependency of varying irradiance.

<table>
<thead>
<tr>
<th>Irradiance level [W/m²]</th>
<th>Slope m</th>
<th>y-intercept n</th>
<th>k [mg/m³/s]</th>
<th>( K_d ) [m²/mg]</th>
<th>Coefficient of determination R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.283</td>
<td>14.8450</td>
<td>0.07</td>
<td>6.50</td>
<td>0.6363</td>
</tr>
<tr>
<td>2</td>
<td>1.392</td>
<td>9.9496</td>
<td>0.10</td>
<td>7.15</td>
<td>0.7524</td>
</tr>
<tr>
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<td>8.2467</td>
<td>0.12</td>
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</tr>
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<td>4</td>
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<td>0.9185</td>
</tr>
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<td>0.19</td>
<td>4.02</td>
<td>0.9567</td>
</tr>
<tr>
<td>7</td>
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<td>4.8082</td>
<td>0.21</td>
<td>3.89</td>
<td>0.9640</td>
</tr>
<tr>
<td>8</td>
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<td>4.3751</td>
<td>0.23</td>
<td>3.64</td>
<td>0.9663</td>
</tr>
<tr>
<td>9</td>
<td>1.155</td>
<td>4.1155</td>
<td>0.24</td>
<td>3.56</td>
<td>0.9693</td>
</tr>
<tr>
<td>10</td>
<td>1.107</td>
<td>3.9059</td>
<td>0.26</td>
<td>3.53</td>
<td>0.9694</td>
</tr>
<tr>
<td>11</td>
<td>1.054</td>
<td>3.7483</td>
<td>0.27</td>
<td>3.56</td>
<td>0.9739</td>
</tr>
</tbody>
</table>

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**Fig. 3.** Regression results of data presented in Table 4 for the photocatalysis of a NOXER paving block (data taken from [19]).

**Fig. 4.** Influence of UV-A irradiance on the reaction rate constant k, tested with constant RH = 50% and \( C_{in} = 1.0 \) ppmv NO.

**Fig. 5.** Influence of UV-A irradiance on the adsorption equilibrium constant \( K_d \), tested with constant RH = 50% and \( C_{in} = 1.0 \) ppmv NO.
the surface and prevent therefore the pollutants to adsorb on the reactive catalyst sites, which also is referred to in [17]. This could lead to the assumption that with increasing humidity the adsorption equilibrium constant \( K_d \) will be decreased. In other words, NO and water vapor can be considered as an additional reactant. For reaction rates on mixtures of VOCs, [12] suggest an extended Langmuir–Hinshelwood model introducing additional reactionants. For the present case this extended expression could consider the influence of humidity. Under consideration of the performed modifications from Eq. (11) the disappearance rate for the reactant NO, \( \tau_{\text{NO}} \), would read:

\[
\tau_{\text{NO}} = \frac{K_d \cdot c_{\text{NO}}}{1 + K_d \cdot c_{\text{NO}} + K_d \cdot c_{\text{H2O}} + \alpha_1 (1 + \sqrt{1 + \alpha_2})}. \tag{12}
\]

The water vapor concentration at 20 °C (experimental condition) is now a function of \( RH \) with \( \alpha_1 = 17.31 \) g/m³ \( K_{d,H2O} \). Furthermore, Eq. (12) can be rewritten as:

\[
\tau_{\text{NO}} = \frac{K_d \cdot c_{\text{NO}}}{1 + K_d \cdot c_{\text{NO}} + \alpha_1 (1 + \sqrt{1 + \alpha_2})}, \tag{13}
\]

with \( K_d \) as effective adsorption equilibrium constant in the presence of water vapor:

\[
K_d = \frac{K_d \cdot NO}{1 + K_d \cdot NO + K_d \cdot H2O + \alpha_1 (1 + \sqrt{1 + \alpha_2})}. \tag{14}
\]

Eq. (13) can be substituted into Eq. (8), which can be integrated, and with Eq. (5), again Eq. (9) is obtained, in which \( k \) is now a function of \( E \) and \( K_d \) of \( RH \).

However, similar measurements as in the previous paragraph but now with varying the relative humidity (RH) in steps of 10% from 10% to 70% (7 × 5 measurement matrix), are not linear in the proposed model. The respective measurements are given in Fig. 6. These results learn that, against earlier expectations, there is no continuous decrease of NO adsorption with rising RH. It rather shows an optimum value of RH where the respective NO adsorption equilibrium achieves highest values. The dependence of \( K_d \) on the RH can be described with a polynomial equation of the second degree which reads as:

\[
K_d = \alpha_4 \cdot RH^2 + \alpha_5 \cdot RH + \alpha_6. \tag{15}
\]

The coefficients \( \alpha_4, \alpha_5 \) and \( \alpha_6 \) have been fitted, and read for the present paving stone −0.001, 0.0802 and 1.63 m³/mg, respectively.

The underlying line fits for all individual measurements are summarized in Table 6. Considering this specific sample, a level of RH at around 40% seems to be advantageous for a preferably high NO adsorption. The adsorption capacity of the pollutant onto the surface seems to be of major influence for the overall degradation performance of the NO. Therefore, a similar dependence of the NO degradation rate on the relative humidity is expected. However, measurements presented in Fig. 7 learn that this is not the case. Here, starting from 10% RH the degradation rate linearly decreases with increasing RH. This refers again the initial assumption of a sole influence of relative humidity on the adsorption equilibrium constant only. To obtain the linear behavior of NO degradation (cp. Fig. 7) while knowing the influence on the adsorption equilibrium constant (cp. Fig. 6) the reaction rate constant must have an influence, though. This is proven by the measurements given in Fig. 8. Considering the experimental data, the influence of the relative humidity on the reaction rate constant \( k \) can be explained by:

\[
k = \alpha_7 \cdot RH^{\alpha_8}. \tag{16}
\]

Again the coefficients \( \alpha_7 \) and \( \alpha_8 \) have been fitted and amount to 1.30 mg/m³/s and −0.42, respectively. The described behavior can be explained by the number of reaction sites which will be occupied by water molecules with increasing RH. Therefore, the more water vapor in the reactor the lower will be the degradation and the reaction rate constant, respectively, because of the lack of free reaction sites.

In conclusion it can be said that Eq. (9) cannot only be used to study the effects of \( C_{\text{NO}} \) and \( Q \), but also \( E \) and \( RH \). From experimental data, \( \alpha_1, \alpha_2, \alpha_7, \) and \( \alpha_6 \) (all governing \( k \)), and \( \alpha_7=\alpha_8 \) (governing \( K_d \)) can be fitted. These fitting parameters finally allow the determination of \( k \) and \( K_d \), which characterize each specific product. Using the

![Fig. 6. Influence of relative humidity on the adsorption equilibrium constant \( K_d \), tested with constant \( E = 10 \text{ W/m}^2 \) and \( C_{\text{NO}} = 1.0 \text{ ppmv NO} \).](image)

![Fig. 7. Influence of relative humidity on the total NO degradation rate, tested with constant \( E = 10 \text{ W/m}^2 \) and \( C_{\text{NO}} = 1.0 \text{ ppmv NO} \).](image)
disappearance rate of a reactant according to Eq. (7) the degradation rate can now be expressed in function of a varying irradiance at the relative humidity of 50% or, the other way around, in function of a varying relative humidity at an irradiance level of 10 W/m². A more complex derivation of the combined influences of irradiance and relative humidity on the disappearance rate is not possible with the present data. Such computations would require more measurement series with varying irradiance at relative humidity levels different from 50% and vice versa with irradiance levels different from 10 W/m².

5. Large-scale application

In general it can be concluded that PCO on concrete paving blocks is a proven reaction process which under controlled laboratory conditions can be highly effective. However, the demonstration of the same in real outside condition still seems to be a crucial point. Therefore, tests outside of the laboratory in a real street situation are necessary. If those tests can be concluded to be successful, their data can be used as input for real-scaled models in order to see whether the laboratory results can be translated to real site measurements.

In the recent past a few real site experiments have been conducted already. A central street for example was paved in Bergamo, Italy in 2006 [22]. Here a total area of 12,000 m² including road and sidewalk were paved with active paving blocks. This project was concluded to be successful. For the 10 h average of three consecutive days a decrease in NOₓ-concentration of up to 30% was measured. Another, noteworthy project was the pavement of the sidewalks and parking lanes of road through the city center of Antwerp, Belgium [21]. Here a total area of 10,000 m² was paved. This project was successfully finished too, but specific data is not available which makes a further assessment difficult. Another major project is conducted now in Paris, France. In this case a heavily frequented road is paved with concrete containing TiO₂ as photocatalyst. Results are not published so far and a final report is expected later this year. There are some other case studies which are not specifically mentioned here. However, it can be concluded that so far no verifiable decrease of NOx pollution can be specified, which originates solely on the action of the PCO provided by the photocatalytic characteristic of the pavement. This has a number of reasons which of the following are attached with greatest importance. In all cases there is no sufficient description of the initial pollutant situation given. This refers to the duration of measurements (possibly all seasons should be incorporated, annual mean) as well as to the positioning of the sample location. Here, especially the dilution of pollutant as a function of the distance to the source has to be accounted for. A representative measurement in the above sense of course also needs to be conducted after the respective surface is supplied with an active paving. Simultaneous comparative measurements need to be carried out in a similar but not treated environment (reference situation). Furthermore, should the location itself also show some aspects regarding the controllability of environmental influences. A “street-canyon” with close or even gap-free house construction in a straight and busy street seems to be favorable. But also the exposure to sunlight as well as the wind direction and velocity need to be considered for an analysis of the data.

Being aware of the insufficiencies of the above examples a new demonstration project was started in the second half of 2008. In the framework of this project a street (170 × 5.5 m²) will be paved with active paving stones in the city of Hengelo, The Netherlands. In order to precisely describe the present situation comprehensive measurements are ongoing. Therefore, a protocol has been developed. The location is in accordance with the demands stated above. The measures which are monitored are the following: temperature, wind speed and wind direction, air pressure, relative humidity, NO concentration, NO₂ concentration, irradiance (visible and UV light), traffic volume, and ozone concentration. The direct measurements of the gaseous air pollutants are carried out at different locations (modified situation and parallel control-street with unchanged pavement) and in different heights above the ground (5 cm, 30 cm and 150 cm) in order to take account for the dilution effect. Furthermore, the measurements cover all seasons with each long lasting individual measurements. This way it is expected to gather valuable information on a large-scale change of the air quality. In addition, the results on the NOₓ degradation in combination with the environmental parameters will be used as an input for computational fluid dynamics simulations (CFD) based on the reaction kinetics explained in the previous paragraph.

6. Conclusions

The heterogeneous photocatalytic oxidation is a promising technique for effectively reducing air pollution in inner city areas where high emissions of nitrogen oxides caused by increasing traffic loads are causing health problems. Besides this, the self-cleaning aspect coming along with PCO should not be ignored either. Concerning this matter, promising results have also been achieved, e.g. by [23,24].

Numerous measurements, also prior to this research project, carried out within the last two years showed that the concentration of nitrogen oxides in the ambient air can be notably reduced by the photocatalytic oxidation using TiO₂ under UV exposition. The experimental data obtained in a reactor provide a basis for the modeling of the degradation process using the Langmuir–Hinshelwood kinetics. The established model now allows for the prediction of the performance of certain air-purifying concrete products under various conditions. Due to the incorporation of the most important influencing boundary conditions namely pollutant concentration, volumetric flow, irradiance and relative humidity, a prediction of the degradation performance in a wide range is possible. Furthermore, now the unique characterization of photocatalytic concrete products is possible by the derivation of its conversion and adsorption rate constants. The derived model also confirms that in the considered reactor the conversion of NOₓ is the rate-determining step in the photocatalytic oxidation of NOₓ. The obtained modeling results are in a good agreement with the lab measurements.

Based on a thorough analysis of PCO on cementitious surfaces and the knowledge of its influencing parameters a reaction kinetics model was derived. With an ongoing on site experiment these models are now transferred to the real scale. Hereby representative measurements with sufficiently long measurement periods at modified as well as control locations are taken into account. For the associated computational fluid dynamics (CFD) calculations, the here derived kinetics will be used as it accounts for the effect of irradiance and relative humidity.
List of Symbols

Roman

B  breadth
C  concentration [mg/m³, mole/mole, ppmv]
D  diffusion coefficient [m²/s]
dh  hydraulic diameter
E  irradiance [W/m²]
h  height [m]
k  reaction rate constant [mg/m³s]
K  diffusion coefficient [m²/s]
λ  wavelength [nm]
M  molecular mass [g/mole]
p  pressure [Pa]
Q  volumetric flow [l/min]
RH  relative humidity
r  disappearance rate of substance x
Sh  Sherwood number
T  temperature [K]
V  volume [m³]
v  velocity [m/s]

Greek

ρ  density [g/cm³]
λ  wavelength [nm]
u  kinematic viscosity [m²/s]

Subscript

con  converted
g  gas
h  hydraulic
NO  nitrogen monoxide
w  wall

Abbreviations

CFD  computational fluid dynamics
FEM  finite element analysis
NOM  natural organic matter
NIST  National Institute of Standards and Technology
PCE  perchloroethylene
PCO  photocatalytic oxidation
TCE  trichloroethylene
VOC  volatile organic compounds

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References