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Adsorption phenomena in photocatalytic reactions: The case of toluene, acetone and heptane

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ABSTRACT

Nowadays, with the increase in the thermal insulation of buildings, indoor air quality (IAQ) has deteriorated, particularly because of the presence of volatile organic compounds (VOC). To improve IAQ, photocatalytic processes can be used. Photocatalytic reactions can be broken down into three steps: adsorption of pollutants, chemical reaction, and desorption of water, carbon dioxide and by-products. In this work, the accessibility of the pollutants to the reactive sites of a commercial TiO₂-photocatalyst is studied. Firstly, adsorption mechanisms are investigated through toluene adsorption isotherms in batch reactors. In humid air conditions (relative humidity of 50% at 24 °C), the classical adsorption models cannot be applied. Consequently, a new model, called the “Langmuir–multi”, is built. It fits the obtained experimental data properly. Adsorption equilibrium constants are calculated based on this new model. To understand adsorption mechanisms better, adsorption isotherms are also performed in dry air conditions with toluene and in humid air with acetone and heptane. It is observed that water vapor plays a major role. Secondly, photocatalytic reactions are carried out with toluene, acetone and heptane in humid air. The kinetic curves are well-represented by the Langmuir–Hinshelwood (L–H) equation so that reaction and equilibrium constants can be assessed. The L–H equilibrium constant appears to depend on the type of pollutant and on the affinity between the pollutant and the photocatalyst surface. No correlation is found between the equilibrium constant and light intensity. It is also shown that the calculated L–H equilibrium constants are not equal to those previously obtained in dark conditions and in batch reactors.

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1. Introduction

Over the past several years, indoor air quality (IAQ) has become an increasingly common preoccupation [1]. IAQ is degraded by several types of pollutant (microbial, particulate and gaseous) that can be found at higher concentrations inside than outside. Among gaseous molecules, volatile organic compounds (VOC) represent the main pollution in closed atmospheres where people spend between 70 and 90% of their time. Indoor VOC concentrations usually range between a few $\mu\text{g m}^{-3}$ up to hundreds of $\mu\text{g m}^{-3}$ [2]. While some VOC may be present at concentrations that are not considered acutely harmful to human health with short-term exposure, long-term exposure may result in mutagenic or carcinogenic

effects, the “sick building syndrome”, asthma and cardiovascular illnesses [3].

Several indoor air purification processes have been developed with the objective of eliminating these compounds. Among the different possible treatments, gas-phase photocatalytic oxidation using TiO₂ as a photocatalyst has been proved to be a convenient innovative technology for the improvement of indoor air quality [4–6]. The photocatalytic process can be used with low pollutant concentrations at a low flow. It is based on the use of a light-activated semi-conductor to speed up VOC oxidation. Electron–hole pairs are photogenerated in the bulk of the semi-conductor by irradiation and move to the particle surface. Electrons reduce electron acceptors such as molecular oxygen. Holes oxidize electron donors including adsorbed water or hydroxyl anions OH[−] to give hydroxyl radicals (OH•). The latter are the primary oxidants in further VOC degradation [7]. The presence of oxygen can prevent the re-combination of electron–hole pairs [8]. Photocatalytic mechanisms are commonly described by three steps: adsorption of

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Table 1

Specific surface area values for the photocatalytic material, titanium dioxide and support constituting the medium.

	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	Porous volume ($\text{cm}^3 \text{g}^{-1}$)	% of pores <50 nm
Photocatalyst	122	0.075	98.5
TiO ₂	194	0.331	91.5
Support (quartz fibers and binder)	33	0.047	89.0

pollutants onto the photocatalyst surface, surface reaction of pollutants, and desorption of water, carbon dioxide and by-products. Although the surface reaction is the main step, it can only occur if the reactive sites are free and accessible. Consequently, adsorption is also a major stage in photocatalytic reactions. In the literature, the accessibility of the pollutants to the reactive sites is generally characterized by the equilibrium constant calculated from the Langmuir–Hinshelwood kinetic model [9]. Some authors have also determined the equilibrium constant by performing adsorption isotherms in the dark [6,9–14]. In most cases, these two equilibrium constants are not equivalent and the experiments designed to compare them are carried out in static reactors and mainly for liquid–solid interactions using a suspension of powdered TiO₂ [11–14].

The work hereafter focuses on the adsorption step in photocatalytic reactions for three pollutants (toluene, acetone and heptane) using a commercialized TiO₂-based photocatalyst. First of all, adsorption equilibrium constants are determined in dark conditions by performing adsorption isotherms in static reactors and adsorption mechanisms are considered. The role of water vapor in these mechanisms is particularly taken into account. In the second part, the three pollutants are photocatalytically oxidized in a dynamic reactor operating in almost real indoor air conditions. The kinetic adsorption constants are evaluated using the Langmuir–Hinshelwood model. These constants are then compared to the dark constants. Finally, the influence of light intensity on the kinetic adsorption constants is discussed.

2. Experimental and methodology

2.1. Photocatalyst

A commercial TiO₂-catalyst constituted of non-woven quartz fibers linked by a patented technology was used in this study (patent # WO03010106). It is composed of titanium dioxide powder (16 g m²) linked on the quartz fiber support using an inorganic binder, whose details cannot be given for reasons of industrial confidentiality. The nitrogen adsorption/desorption isotherms were measured at 77 K with a Micrometrics ASAP 2010 surface analyzer for the photocatalytic material in comparison with the TiO₂ and the support (quartz fibers and binder) constituting this material. The specific surface area was calculated from the N₂ adsorption isotherm by the Brunauer–Emmett–Teller equation, and mesopore and micropore volumes were estimated according to the Barrett–Joyner–Halenda and Horwath–Kawazoe theories, respectively. Data are presented in Table 1. Only values for the specific surface area, the porous volume and % of pores with diameters less than 50 nm are given in order to respect industrial confidentiality.

The specific surface area of the photocatalyst used in this study is above 100 m² g⁻¹. It develops a majority of pores with diameters less than 50 nm. The porous volume was found equal to 0.075 cm³ per gram of photocatalytic medium. In the kinetic study, the photocatalyst was used as a filter perpendicular to the air flow.

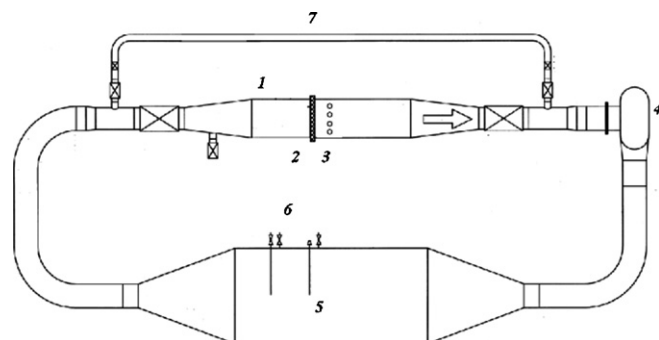


Fig. 1. Geometry of the dynamic photocatalytic reactor: (1) principal reactor, (2) TiO₂ photocatalytic medium, (3) UV lamps, (4) fan, (5) air tranquilization chamber, (6) sampling points, (7) by-pass.

2.2. Chemicals

The volatile organic compounds (>99% purity) were purchased from Aldrich Chemicals. They were used directly as received.

2.3. Adsorption isotherms

To study the adsorption mechanisms of the three VOC on the photocatalyst, adsorbate/adsorbent equilibrium properties were assessed by conducting adsorption isotherms in batch reactors. Before each experiment, the photocatalyst was irradiated under UV (photon flux of 6 mW cm⁻²) for at least 2 h. Then, it was oven-dried at 160 °C for 48 h. When dry air was required, reactors were ventilated with compressed purified dry air. When water vapor was needed, liquid water was added using a syringe. A 0.6 g sample of photocatalyst was introduced into the 2L-reactor placed in a thermostatic bath regulated at 24 ± 2 °C. A precise volume of volatile organic compound was injected by means of a syringe through the septum of the reactor in order to obtain the required initial concentration (C_0 ranging from 0.54 to 10.85 mmol m⁻³).

Previous kinetic experiments have shown that equilibrium is achieved after 48 h. When equilibrium was reached, 80 μL of the batch reactor atmosphere was sampled with an airtight syringe and analyzed using a gas chromatograph (PerkinElmer Autosystem XL) equipped with a flame ionization detector (FID).

An adsorption isotherm curve represents the adsorbed quantity of pollutant by unit surface area of material at equilibrium (q_e , mmol m⁻² catalyst) as a function of the pollutant concentration in the gas phase at equilibrium (C_e , mmol m⁻³). The quantity of adsorbed pollutant can be calculated for each initial concentration C_0 by the following relation:

$$q_e = \frac{(C_0 - C_e)V}{S} \quad (1)$$

where V is the reactor volume (m³) and S is the catalyst surface area (m²). To respect confidentiality, dimensionless results are given. The results on toluene are considered as the reference. Adsorption capacities are divided by the maximum adsorption capacity obtained for toluene.

2.4. Dynamic photocatalytic reactor

A dynamic photocatalytic reactor was specially constructed as described in a previous paper [15]. It is composed of a recycling loop shown in Fig. 1. The loop includes the principal reactor with the photocatalyst and four lamps (PL-S, 9 W, Philips, 365 nm or 254 nm) at its center, a centrifugal fan (VSB14-4 T, ATIB) and an air tranquilization chamber.

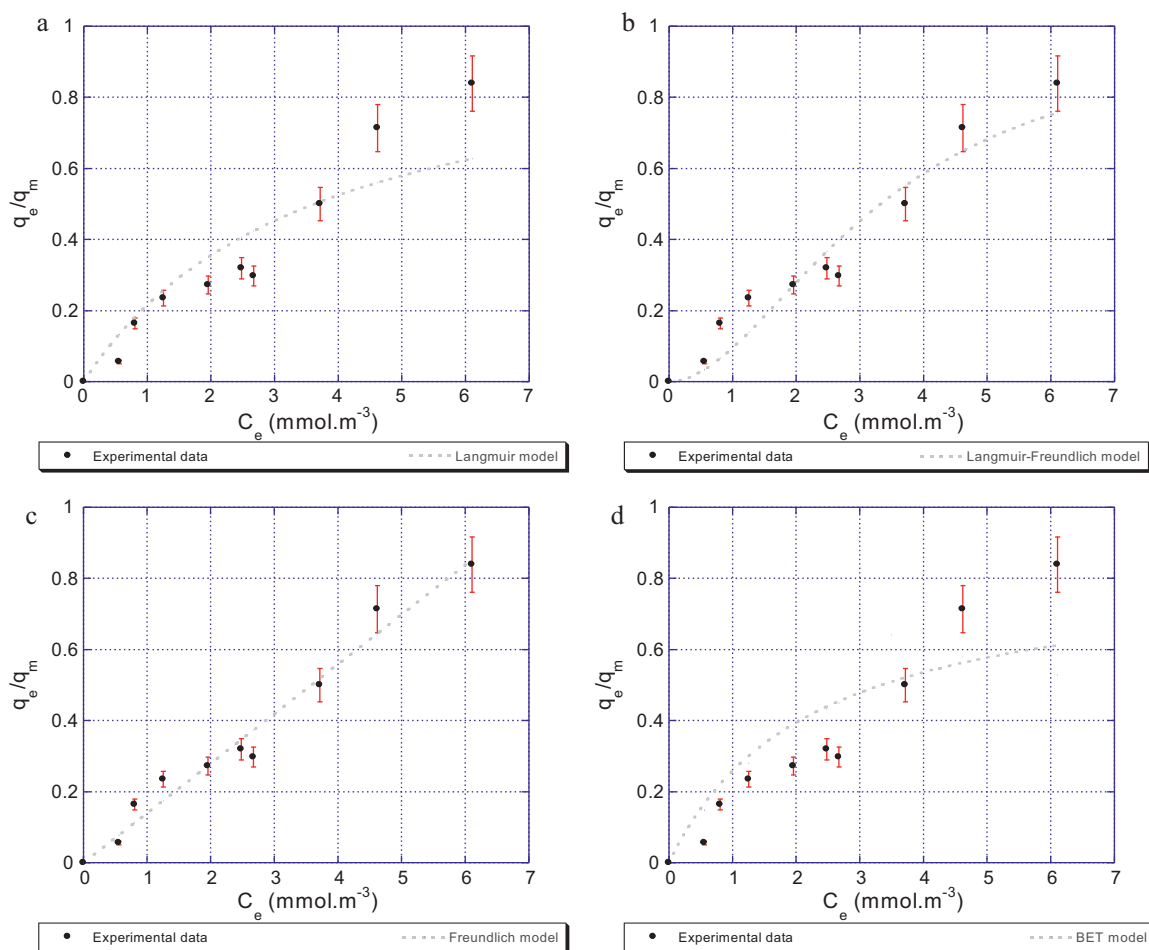


Fig. 2. Examples of adsorption isotherm curves obtained for toluene in humid air conditions and fitting of the Langmuir (a), Langmuir–Freundlich (b), Freundlich (c) and BET (d) models to the experimental results.

The geometry of this device was optimized in order to ensure a homogeneous flow field, photon flux and concentration over the entire photocatalyst surface [15]. The UV photon flux was mapped and an average intensity of received irradiation was calculated. For each experiment, the flow rate was $150 \text{ Nm}^3 \text{ h}^{-1}$, the total mass of catalyst was 3.75 g (i.e. 400 cm^2) and the total volume of the reactor was 420 L . Two grids held the photocatalytic medium in position. The four lamps were placed to provide an average light irradiation of up to 4 mW cm^{-2} . Two UV wavelengths were used separately: UVA (365 nm) and UVC (254 nm). Before collecting data, the photoreactor was conditioned for 1 h with a feed stream of humid air (50% at 24°C). Then, the recycling loop was closed, the by-pass was opened, the principal reactor was closed and the lamps were switched on. A precise volume of VOC was injected by means of a syringe through the septum of the air tranquilization chamber ($C_0 = 0.2\text{--}0.4 \text{ mmol m}^{-3}$ or $5\text{--}10 \text{ ppm}$). In this configuration, a homogeneous concentration was obtained after 15 min . At that time, the by-pass was closed and the principal reactor was opened. The VOC and carbon dioxide concentrations were followed using a gas chromatograph with a flame ionization detector and a catharometer, respectively. The sampling was done every 3 min .

3. Results and discussion

3.1. Mechanisms of adsorption

To understand and compare adsorption mechanisms onto the TiO_2 -based photocatalyst, adsorbate/adsorbent equilibrium prop-

erties were evaluated in dark conditions. First of all, adsorption properties were determined by performing adsorption isotherms of toluene, which is a typical indoor air molecule present at relatively high concentrations with values near $0.5 \text{ } \mu\text{mol m}^{-3}$ [2]. Then, some experiments were carried out with two other molecules, acetone and heptane, in order to assess the role of the hydrophilicity of the organic substrate in adsorption mechanisms.

3.1.1. Adsorption isotherms of toluene in humid air

The methodology described in paragraph 2.3 was applied three times for toluene in humid air (50% at 24°C). Fig. 2 displays the results corresponding to one of the adsorption isotherms. It can be observed that the isotherm curve exhibits a two-step-like behavior with an inflexion point around a toluene concentration in the gas phase of $C_{\text{inf}} = 3 \text{ mmol m}^{-3}$. This two-step-like behavior is consistent with previous studies for which this particular shape reflects the different strengths of the interaction of the target compounds with two surface centers [5,16]. A non-linear least squares regression function was used to fit the experimental results to classical adsorption models (Table 2). One of them is the Langmuir model, which relies on the hypotheses that the catalyst surface is uniform and that there is only one kind of adsorption site [17]. To take into account the possible heterogeneity of the surface, there are two other models derived from the Langmuir equation: the Langmuir–Dual Site equation and the Langmuir–Freundlich equation [5,16,18]. The empirical Freundlich equation conveys the variation in adsorption energies with the quantity of adsorbed pollutant. This variation in energies is justified by the hetero-

Table 2

Usual adsorption models and determination coefficients between each model and the experimental data.

Model name	Main hypotheses	Equation	r^2
Langmuir	Homogeneous monolayer adsorption	$q_{eL} = \frac{q_m b C_e}{1 + b C_e}$	0.761
Freundlich	Heterogeneous surface and intermolecular interactions	$q_{eF} = K C_e^{1/n}$	0.986
Langmuir–Dual Site	Several types of adsorption site	$q_{eLD} = \sum_i q_{mi} \frac{b_i C_e}{1 + b_i C_e}$	0.972
Langmuir–Freundlich	Several types of adsorption site	$q_{eLF} = q_m \frac{(b C_e)^n}{1 + (b C_e)^n}$	0.936
Co-adsorption	Competitive adsorption between species	$q_{eCoads} = q_m \frac{b_A C_A}{1 + \sum_i b_i C_i}$	0.761
BET	Multilayer adsorption	$q_{eBET} = \frac{q_{mono} \alpha' \frac{C_e}{C_{sv}}}{\left(1 - \frac{C_e}{C_{sv}}\right) \left[1 + (\alpha' - 1) \frac{C_e}{C_{sv}}\right]}$	0.824

¹ q_m , maximal adsorption capacity of the medium; b , equilibrium constant.

² K, n , empirical constants of the model.

³ q_{mono} , maximal adsorption capacity of the first adsorbed layer, α' = constant of the model, C_{sv} = concentration of the pollutant saturated vapor.

generity of the adsorbent surface and by possible intermolecular interactions (multilayer adsorption) [19]. In the case of the simultaneous presence of compounds in the gas phase, the co-adsorption equation can be used [20]. In the present work, a competitive adsorption can take place between toluene and water molecules. The Brunauer–Emmett–Teller (BET) model, assuming a multilayer adsorption, can also be tested. The latter relies on the hypotheses that each adsorption site is available for only one molecule and that the adsorption surface is homogeneous [21].

According to the determination coefficients r^2 presented in Table 2, it can be concluded that none of the tested models fits the experimental data properly. As shown in Fig. 2, since the adsorption of toluene in humid air does not reach a steady-state value, the Langmuir isotherm does not satisfactorily represent the obtained results. Furthermore, it is not possible to dissociate the results obtained with the co-adsorption model from those calculated by the Langmuir equation. This can be attributed to the fact that the adsorption of water vapor into the photocatalytic medium was not followed during the experiment so that the concentration of water in the gas phase was considered constant. The Langmuirian equation for adsorption on two sites having different strengths does not give satisfactory results either. Although the determination coefficient appears satisfactory, the values of the constants are not consistent. The BET model, which accounts for multilayer adsorption, also does not match the constant increase in adsorbed toluene. The best determination coefficient is obtained with the Freundlich model. However, the Freundlich isotherm curve does not represent the two-step-like behavior of the experimental toluene adsorption isotherm.

Following on from the above remarks, a new model, called the “Langmuir-multi”, was built and fitted to the experimental data. In this model, it is considered that the first part of the curve corresponds to a homogeneous monolayer adsorption and that several mechanisms are involved in the second part of the curve, such as the presence of heterogeneous sites, multilayer adsorption and other possible occurring phenomena. According to these hypotheses, the Langmuir equation was kept for the first part of the curve (Eq. (2)) and for higher C_e , the Langmuir–Freundlich equation, taking into account different possible mechanisms overall, was applied (Eq. (3)):

The equation of this new model is given below:

$$\text{For } 0 \leq C_e \leq 3 \text{ mmol m}^{-3}, \quad q_e = \frac{q_{m1} b_1 C_e}{1 + b_1 C_e} \quad (2)$$

$$\text{For } C_e \geq 3 \text{ mmol m}^{-3}, \quad q_e = q_{m1} \frac{b_1 C_e}{1 + b_1 C_e} + q_{m2} \frac{b_2 (C_e - C_{inf})^n}{1 + b_2 (C_e - C_{inf})^n} \quad (3)$$

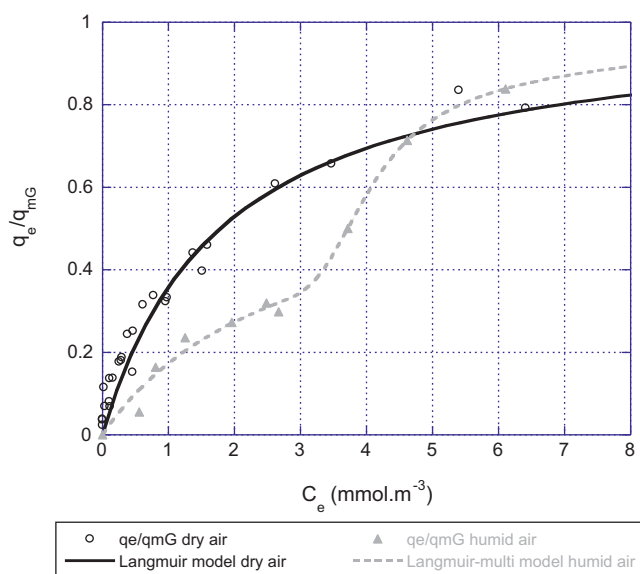


Fig. 3. Adsorption isotherms of toluene in humid and dry air conditions.

where b_1 and b_2 are the adsorption constants ($\text{m}^3 \text{mmol}^{-1}$ and $\text{m}^{3n} \text{mmol}^{-n}$, respectively), and q_{m1} and q_{m2} are the maximum adsorption capacities (mmol m^{-2}).

With this “Langmuir-multi” model, the calculated determination coefficients r^2 reach about 0.99. However, it only allows comparisons between experiments to be made and not adsorption mechanisms to be really understood. Due to the special shape of the isotherm curve, it can be assumed that additional phenomena occur, including the dissolution of toluene in water clusters formed on the catalyst surface [22].

3.1.2. Adsorption isotherms of toluene in dry air

To assess the role of water vapor in the adsorption mechanisms involved, isotherm experiments were also conducted in dry air (2% relative humidity at 24 °C). The experimental data for both humid and dry air conditions are plotted in Fig. 3. Thus, in dry air, the isotherm curves present a different shape from those obtained under humid air conditions revealing that adsorption mechanisms are not similar and confirming that water certainly plays a major role. In dry air conditions, the experimental data are well represented by the Langmuir equation over the whole range of equilibrium concentrations C_e .

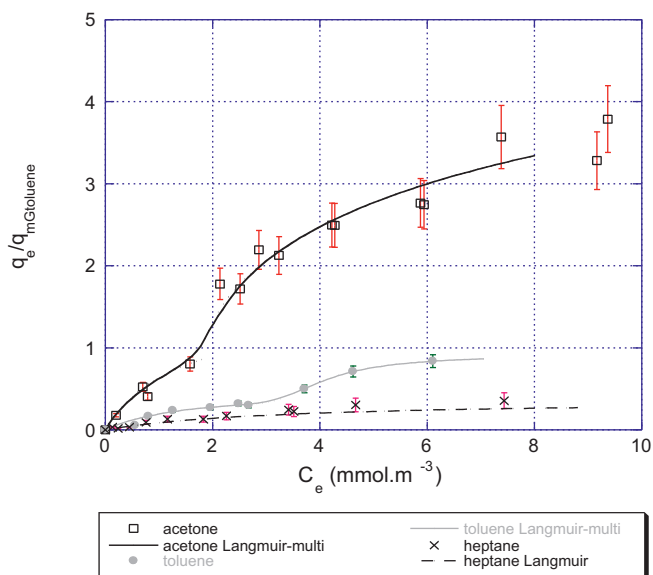


Fig. 4. Adsorption isotherms of toluene, acetone and heptane in humid air (RH = 50% at 24 °C).

According to the results obtained, it can be seen that water vapor significantly affects the adsorption behavior of the photocatalytic medium. The observed difference can be attributed to the formation of a layer of water clusters in humid air conditions. The presence of a film of water depends on the texture and surface characteristics of the TiO₂ samples [22]. Cao et al. [23] have shown that TiO₂ is strongly hydrophilic generating a preferential adsorption of water. However, TiO₂ is not the only hydrophilic component of the photocatalytic medium. According to Goss and Schwarzenbach [24], a quartz surface can also be considered a hydrophilic mineral surface. They concluded that the adsorption properties of a hydrophilic mineral surface for organic vapors are dominated by the presence of a film of adsorbed water. This film may be composed of one or several layers of water clusters decreasing accessibility to active sites. So it is possible that the apparent adsorption constant is mostly the consequence of the diffusion and dissolution of the pollutant into the liquid and may depend on the hydrophilicity of the organic substrate, which defines the extent of its interaction with adsorbed water on the TiO₂ surface.

3.1.3. Adsorption isotherms of three pollutants with different solubilities in humid air

To confirm the presence of a film of water when working in humid air conditions, three pollutants with different aqueous solubilities were tested. Adsorption isotherms were carried out for toluene, acetone and heptane in humid air (50% relative humidity at 24 °C). Acetone is infinitely soluble in water. The solubility of toluene is 5.75 mmol l⁻¹ at 25 °C whereas heptane is not soluble in water [25]. Fig. 4 displays the corresponding results.

As seen in Fig. 4, the adsorption isotherms of both acetone and toluene can be fairly well described using the Langmuir-multi model whereas the adsorption isotherm of heptane is better rep-

Table 4

Maximal quantity of possibly absorbed acetone and toluene and comparison with the maximal adsorption capacity q_{mG} .

	Q_{abs} (mmol)	q_{abs}/q_{mG} (%)	q_{m2}/q_{mG} (%)
Toluene	0.0003	2.5	42.0
Acetone	0.0049	58.9	77.0

resented by the Langmuir equation. The calculated Langmuir and Langmuir–Freundlich constants for the three pollutants are listed in Table 3.

Considering the overall adsorption capacity for toluene ($q_{mGtoluene} = q_{m1toluene} + q_{m2toluene}$) as a reference, it is found that the medium presents the highest adsorption capacity for acetone followed by toluene and heptane. So, it appears that the higher the hydrophilicity, the higher the sorption capacity. At this stage, these experiments lead to the conclusion that the formation of a film of water at the catalyst surface in humid air conditions is credible. Monolayer adsorption and absorption phenomena seem to co-exist in the second part of the isotherm curve.

Considering the value of the relative humidity in the reactors, the maximum amount of water that could be collected by the medium was calculated. The obtained value of 21 mg corresponds to an occupied volume of condensed water less than the available porous volume of the medium. Then, for further calculations, it was supposed that all the initial water content in the gas mixture was adsorbed and condensed in a film of water partially filling the pores of the photocatalytic medium. From Henry's law, the maximal quantity of acetone and toluene that could be absorbed (Q_{abs}) into the layer of water clusters was evaluated. Henry's law is expressed by Eq. (4) below:

$$C_s = p.H \quad (4)$$

where C_s is the saturated concentration in the aqueous phase, p is the partial pressure of the compound in the gas phase and H is Henry's constant ($H_{heptane} = 0.0012 \text{ mol l}^{-1} \text{ bar}^{-1}$, $H_{acetone} = 30 \text{ mol l}^{-1} \text{ bar}^{-1}$, $H_{toluene} = 0.15 \text{ mol l}^{-1} \text{ bar}^{-1}$). The results are summarized in Table 4. The maximal quantity of pollutant dissolved in water is called Q_{abs} and is expressed in mmol. When this value is divided by the surface area of photocatalyst involved, it is noted q_{abs} (mmol m⁻²).

In Table 4, the ratio q_{abs}/q_{mG} represents the maximal quantity of pollutant dissolved in the water layer over the maximum adsorption capacity estimated by the Langmuir-multi model. The ratio q_{m2}/q_{mG} gives an idea of the importance of the second part of the isotherm curve in the total sorption capacity of the photocatalytic medium. These two ratios can be compared. In the case of acetone, q_{abs}/q_{mG} and q_{m2}/q_{mG} are close indicating that the second part of the isotherm curve could correspond to a mechanism of absorption. However, in the case of toluene, the difference between the two values is huge. Consequently, it can be concluded that the sorption of VOC onto the photocatalytic medium used in this study is governed by several phenomena, among which the dissolution of species into a layer of water clusters cannot be rejected but is not sufficient to explain the experimental results obtained.

Table 3

Langmuir and Langmuir–Freundlich constants of toluene, acetone and heptane for RH = 50% at 24 °C.

	Langmuir model	Langmuir–Freundlich model			
	$q_{m1}/q_{mGtoluene}$ (mmol m ⁻² catalyst)	b_1 (m ³ mmol ⁻¹)	$q_{m2}/q_{mGtoluene}$ (mmol m ⁻² catalyst)	b_2 (m ³ⁿ mmol ⁻ⁿ)	n
Toluene	0.59 ± 0.06	0.42 ± 0.05	0.41 ± 0.02	1.28 ± 0.50	2.1 ± 0.71
Acetone	1.49 ± 0.11	0.75 ± 0.11	5.01	0.09	0.6
Heptane	0.37 ± 0.16	0.31 ± 0.23	–	–	–

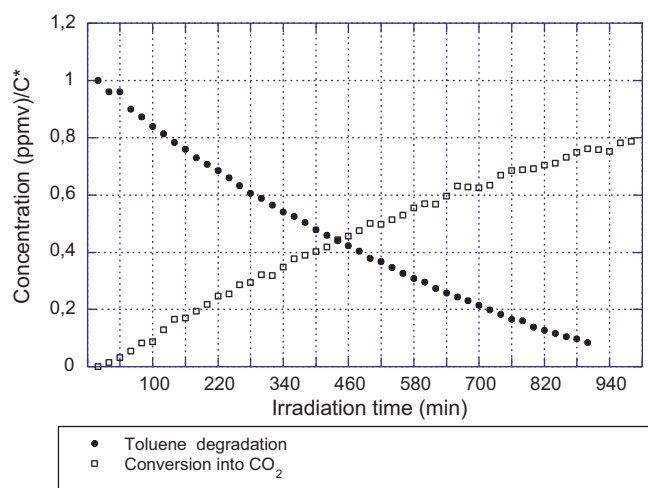


Fig. 5. Photocatalytic degradation of toluene and conversion into CO_2 (values given in relative concentration, C^* : initial concentration).

Table 5
Langmuir–Hinshelwood constants of toluene, acetone and heptane for RH=50% at 24 °C.

	K/K_{toluene}		K_{11}/K_{12}	K_{11}/b_1
	I_1	I_2		
Toluene	1.00 ± 0.13	1.00 ± 0.14	1.04	8.8
Acetone	0.31 ± 0.02	0.29 ± 0.02	1.15	1.6
Heptane	0.47 ± 0.07	0.58 ± 0.07	0.84	5.6

3.2. Heterogeneous photocatalytic process in the dynamic reactor

The photocatalytic oxidation of toluene, acetone and heptane was carried out for two light intensities I_1 and I_2 ($I_1 > I_2$) and in humid air conditions. An example of the photocatalytic degradation of toluene and its proportional conversion into CO_2 is given in Fig. 5 for one of the set of experiments.

The Langmuir–Hinshelwood–Hougen–Watson approach [26] is often used to determine rate laws for such a heterogeneous catalytic mechanism. The approach developed here assumes that the rate-limiting step is the reaction between adsorbed species (oxygen and organic molecules) and the amount of oxygen is regarded as constant. The following equation was applied to the experimental data in order to consider adsorption equilibria:

$$r_0 = k \frac{KC_0}{1 + KC_0} \quad (5)$$

where r_0 is the initial pollutant degradation rate ($\text{mmol m}^{-3} \text{min}^{-1}$), C_0 is the initial pollutant concentration (mmol m^{-3}), k is the reaction kinetic constant ($\text{mmol m}^{-3} \text{min}^{-1}$) and K is the equilibrium adsorption constant ($\text{m}^3 \text{mmol}^{-1}$). This relation is only valid at the initial stage of the photocatalytic reaction, when it can be assumed that no intermediates have already been formed and released into the gas phase. During the kinetics, some intermediates may be formed and their KC terms should be included in the Langmuir–Hinshelwood rate equation even if their adsorption on the TiO_2 surface is rather weak [8]. Equilibrium constants were calculated for the three organic compounds. The value obtained for toluene was taken as a reference. The ratios K/K_{toluene} are reported in Table 5 for the three pollutants under the two levels of light intensity.

First of all, it can be seen from Table 5 that there is no significant influence of light intensity on the equilibrium constants. This observation is in contrast with the results previously obtained in a study carried out by Xu and Langford in which the equilibrium

adsorption constant was shown to drop when the light intensity was increased [11].

Secondly, it is also possible to compare the Langmuir adsorption constants obtained from the kinetic data, K_{11} , and those derived from the corresponding isotherms considering the Langmuir monolayer model, b_1 . For the three studied pollutants, the adsorption constants obtained from the Langmuir–Hinshelwood kinetic model are larger than those obtained from the adsorption isotherms. This is in accordance with several previous studies. Actually, in most cases, the two equilibrium constants are not equivalent [8], the dark equilibrium constant generally being smaller than the equilibrium constant derived from the kinetic study [9]. Coronado et al. found that, for acetone, the K constants are considerably higher than the b constants for several levels of relative humidity using TiO_2 sol–gel deposited onto borosilicate glass cylinders or rings and a recycling loop photocatalytic reactor [5]. Bouzaza and Laplanche [10] obtained a similar result for toluene using a photocatalyst constituted of TiO_2 pellets deposited on glass fibers. In some cases, the inverse behavior is observed. For instance, Railard et al. found K/b ratios lower than 1 using methyl ethyl ketone (MEK) as the organic target and four different photocatalysts [6]. These results were attributed to the fact that not all the adsorption sites were irradiated so they did not all participate in the photocatalytic reactions. Bouzaza and Laplanche [10] also presented similar results for two other photocatalysts used for the photocatalytic degradation of toluene. Coronado et al. [5] stated that, for methyl isobutyl ketone (MIBK), adsorption constants obtained from the Langmuir–Hinshelwood kinetic model are slightly lower than those calculated from the adsorption isotherms. Very different results have been observed concerning the study of adsorption phenomena involved in photocatalytic reactions. It seems that the material used to support TiO_2 is a major element in explaining the differences between these studies. Supports constituted of glass and favorable to the transmittance of light seem to lead to higher K/b ratios. Several hypotheses can be formulated to explain why the two adsorption constants K and b are not equal. Most authors have suggested that, under irradiation, the redistribution of electrons can affect the surface interaction between the substrate and the catalyst as well as the possible retention of the intermediates formed on the catalyst surface [14]. Other authors have attributed these results to the fact that the effect of the temperature on the kinetic adsorption constants has not been fully considered, as the lamps may be able to generate a local increase in temperature [27]. An artifact of the chosen kinetic model could also be responsible for the difference obtained between the two equilibrium constants [5]. Another possible explanation concerns the difference in mass transfer of organic compounds to the medium due to the different reactors used to perform the dark adsorption study (magnetic stirring in 2 L-reactors) and the photocatalytic degradation (dynamic pilot with an inlet velocity of 0.6 m s^{-1}).

4. Conclusion

The adsorption of pollutants onto the photocatalyst surface is one of the main steps in photocatalytic reaction mechanisms. In this study, a TiO_2 -photocatalyst constituted of non-woven quartz fibers, linked together using a patented technology, was studied in terms of VOC adsorption. In humid air (RH=50% at 24 °C), no well-known adsorption models could be satisfactorily applied. Consequently, a new model, called the Langmuir-multi, was used to represent adsorption mechanisms of VOC onto this photocatalyst. An assumption was made that additional phenomena play a role in adsorption, for instance: competitive adsorption between water and VOC, VOC dissolution in water, and several adsorption sites. To check some of these hypotheses, other adsorption isotherms

were carried out: adsorption of toluene in dry air and adsorption of several pollutants with different solubilities in humid air. These experiments indicate that water plays a major role in adsorption mechanisms. Furthermore, a film of water seems to be present when working under humid air.

In the second part of the study, photocatalytic degradation kinetics were performed in a dynamic pilot for toluene, acetone and heptane. These results were modeled with the Langmuir–Hinshelwood equation at the initial time. The Langmuir–Hinshelwood equilibrium constants (K) were calculated. It was shown that they do not depend on light intensity. The equilibrium adsorption constants (K) were compared with adsorption constants in dark conditions (b). It was found that, under irradiation, adsorption constants (b) were higher. To explain this observation, it is suggested that the affinity between pollutant and surface changes with the redistribution of electrons at the photocatalyst surface. Furthermore, the TiO_2 support is presumed to influence the ratio between adsorption constants (K/b).

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