

Kinetic study of ketones photocatalytic oxidation in gas phase using TiO₂-containing paper: effect of water vapor

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Abstract

Photocatalytic oxidation of two ketones, acetone, and 2-butanone, over TiO₂-containing paper was studied under two different levels of relative humidity. Adsorption of these ketones on TiO₂-containing paper is significantly affected by the presence of water vapor. Adsorption isotherms of both acetone and 2-butanone, under dry and humid atmosphere, can be satisfactory described using the Langmuir adsorption model for concentrations ranging from 0 to 6 g m⁻³. Kinetic data of the photocatalytic oxidation of these ketones are analyzed using the Langmuir–Hinshelwood model except for the photocatalytic oxidation of acetone in humid air conditions where adsorption was assumed to be the rate limiting step. In the case of acetone, photoactivity is greatly inhibited in presence of water vapor. On the other hand, it is showed that water vapor has little effect on 2-butanone photocatalytic degradation. The latter is just slightly improved in humid air conditions for initial 2-butanone concentrations upper than 2 g m⁻³. An explanation is given in term of adsorption affinity of the pollutants compared with competitive adsorption of water molecules with the ketones onto TiO₂-containing paper.

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1. Introduction

Indoor pollution has currently become major public concern since it has been observed that people usually spend between 70 and 90% of their time indoor [1–9]. Indoor air quality (IAQ) is governed by numerous factors among which outside air quality, aeration systems, human and animal metabolisms, furniture and materials, and inhabitants or workers activities (cleaning, cooking, smoking, etc.) are there [2,9–11]. Among the detected pollutants in indoor atmospheres, volatile organic compounds (VOC) stood high on the list [7,8,12]. Concentrations of VOC are often significantly higher in indoor air than outdoor [1,4,12–14]. Moreover, these compounds are directly related to human health [2,7]. While some VOC may be present at concentrations that are not considered acutely harmful to human health with short-term exposure, a long-term exposure may result in mutagenic or carcinogenic effects and “sick building syndrome” (headache, respiratory tracts, irritations of eyes, etc.), asthma and cardiovascular illnesses [6,8,14]. The common way to minimize harmful effects of these compounds is to reduce

their concentrations. Numerous treatments exist to remove VOC from the air but these are essentially applicable to the refining of industrial gaseous effluents and not to indoor air purification [15]. During the last 10 years, some studies have focused on the photocatalytic oxidation of VOC in gas phase and the obtained results are encouraging. Photocatalytic oxidation is based on the use of a light-activated semiconductor to speed up VOC oxidation. A semiconductor is a compound which contains a crystalline phase and is able to release some electrons. It is characterized by a band gap of low energy between the valence band and the conduction band. When a semiconductor is irradiated with photons of the appropriate wavelength and energy, the band gap is exceeded and an electron is promoted from the valence band to the conduction band. The resultant electron–hole pair has a lifetime that enables it to participate in chemical reactions. These reactions result in the formation of highly reactive species that can oxidize VOC adsorbed on the catalyst surface [15–19].

There is considerable research on TiO₂ photocatalysis for the removal of harmful organic pollutants from water and air [18,20–22]. Nevertheless, the efficiency of photocatalytic processes in the gas phase has to be improved. Numerous studies dealt with the use of TiO₂-based photocat-

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alysts in the form of powder or pellets [23,24]. This form of TiO₂ involves several technical problems for an application such as purification of indoor air, particularly because it needs a step of filtration after the reaction. For this reason, supported TiO₂ was developed. Generally, a thin layer of TiO₂ is coated on various supports (glass plates, silicon wafers, zeolites, ceramic membranes, activated carbon fiber) [17,25–36]. Only few works were performed on paper as support for TiO₂. Matsubara et al. [37] developed TiO₂-containing papers with various TiO₂ loads and investigated their photocatalytic activity by measuring the decomposition of gaseous acetaldehyde under illumination from a weak UV light source (0.08 mW cm⁻²). Bouzaza and Laplanche [38] compared different TiO₂ supports (TiO₂ pellets deposited on glass fibers, mixed TiO₂-SiO₂ deposited on a tissue and mixed TiO₂-SiO₂ deposited on a cellulose support) for the photocatalytic degradation of toluene in gas phase.

The purpose of the present work is to study the efficiency of photoactive TiO₂-containing paper for the degradation of ketones in the gas phase. Acetone and 2-butanone are typical indoor air pollutants [39]. TiO₂ supports were tested in a batch photocatalytic reactor at a fixed temperature. Attention was particularly focused on the effect of initial pollutant concentrations and on the effect of water vapor on the efficiency of this photocatalytic material.

2. Experimental

2.1. Catalyst

The catalyst was composed of mixed TiO₂ and SiO₂, with an atomic ratio Ti/Si equals to 2/3, deposited on a non-woven support. This support was constituted of cellulose and synthetic fibers bound together with an organic mixture. Titanium dioxide was of anatase crystalline form and the amount of deposited TiO₂ was about 20 g m⁻². The BET surface area was measured by N₂ adsorption with a Micromeritics apparatus (ASAP 2010) and was found equal to 143.5 m² g⁻¹. The N₂ isotherm plot showed an adsorption of fundamental type on a non-porous or a macroporous solid with the presence of mesopores where an anticipated condensation takes place.

2.2. Photocatalytic reactor

The photocatalytic activity of the TiO₂ deposited on cellulose substrates was evaluated by degradation of acetone and 2-butanone in gas phase at a fixed temperature of 30 °C. Acetone and 2-butanone was purchased from Aldrich and their purity was 99 and 99.5%, respectively. They were used directly as received.

Fig. 1 shows a diagram of the 12-L reactor used in this study. UV irradiation was provided by a medium pressure mercury lamp (Heraeus TQ 718 Z4, 700 W, λ_{max} = 365 nm)

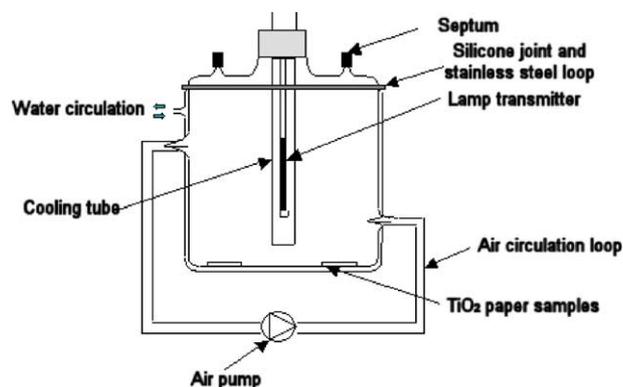


Fig. 1. Photocatalytic batch reactor.

refrigerated by a water flow circulating in a cooling tube around it and placed inside the reactor. The temperature was avoided to increase inside the reactor using a water circulation on the outer side and was measured at different points with thermocouples. Relative humidity was fixed at 30% at 30 °C for humid air and between 0 and 3% for dry air. The relative humidity was controlled with a thermohygrometer at the beginning of each experiment. The gas was mixed in the reactor with a circulating loop fed with an all-Teflon pump (flow of 10 L min⁻¹). The pollutants were introduced in the system as a liquid by a septum on the top of the reactor and were immediately volatilized. A gas chromatograph associated with a flame ionization detector (GC-FID) was used to follow acetone and 2-butanone concentrations and possible by-products formation during kinetics. Gas samples were withdrawn with airtight syringes. Reference runs were conducted with no light activation (adsorption) and with no photocatalyst (photolysis). The photolysis runs lead to the degradation of 20% of 2-butanone within 240 min ($C_0 = 0.7, 3.4$ or 6.9 g m⁻³, RH = 0% or 30%) and 10% of acetone within 270 min ($C_0 = 0.5$ g m⁻³, RH = 50%).

3. Results and discussion

3.1. Acetone degradation

3.1.1. Adsorption isotherms of acetone on TiO₂-paper

Adsorption isotherms were performed under dry and humid atmosphere at a fixed temperature of 30 °C under dark conditions. Equilibrium concentrations were measured with the GC-FID as for kinetics experiments. Fig. 2 displays the results corresponding to the adsorption of acetone in dry and humid air. Circles represent experimental data and solid lines represent the single-site Langmuir isotherm model for C_e ranging from 0 to 6 g m⁻³. The Langmuir adsorption model is defined by Eq. (1):

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad (1)$$

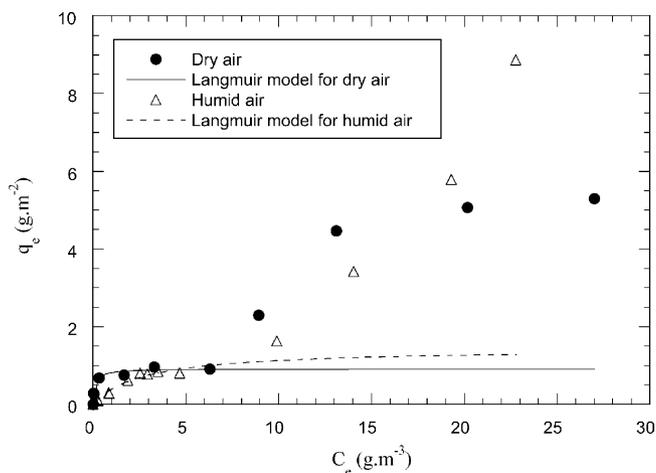


Fig. 2. Adsorption isotherm plots of acetone on TiO_2 -paper in dry and in humid air conditions (solid and dash lines represent the Langmuir adsorption model for C_e ranging from 0 to 6 g m^{-3} under humid and dry atmosphere, respectively).

where q_e is the quantity of adsorbed pollutant by external surface of the catalyst at the equilibrium (g m^{-2}), C_e the equilibrium concentration of the pollutant in gas phase (g m^{-3}), b the adsorption constant ($\text{m}^3 \text{g}^{-1}$), and q_m is the maximum adsorption capacity (g m^{-2}).

The adsorption isotherms of acetone on TiO_2 -paper show a dual distribution that may reflect the difference strength of the interaction of acetone molecules with adsorption sites present at the catalysts surface. It is generally assumed that two types of sites coexist: Ti^{4+} and OH^- [40]. In the present work, kinetic study was performed for initial acetone level comprised between 0.6 and 6 g m^{-3} . On this concentration range, the single-site Langmuir isotherm equation is well fitted. Adsorption parameters for single-site Langmuir model are summarized in Table 1. They indicate that, with increas-

Table 1

Langmuir adsorption isotherm parameters in dry and humid air conditions for C_e ranging from 0 to 6 g m^{-3} for acetone and 2-butanone

	Dry air	Humid air
Acetone		
q_m (g m^{-2})	0.91	1.43
b ($\text{m}^3 \text{g}^{-1}$)	8.75	0.37
R^2	0.9724	0.9638
2-Butanone		
q_m (g m^{-2})	1.74	1.31
b ($\text{m}^3 \text{g}^{-1}$)	4.66	0.85
R^2	0.9939	0.9938

ing relative humidity, the equilibrium adsorption constant b , drops significantly. This observation suggests that in presence of water vapor the formation of a layer of physisorbed water hinders the access of acetone molecules to the adsorption sites.

3.1.2. Photocatalytic oxidation of acetone under dry atmosphere

Fig. 3 shows the variation of acetone concentration ($\ln(C/C_0)$) with the reaction time for five different initial levels. The reaction rate constants of pseudo-first-order kinetic (k_1) was calculated by linear plot of $\ln(C/C_0)$ versus t (Fig. 3). The values of k_1 as a function of C_0 are summarized in Table 2.

The pseudo-first-order reaction rate constant (k_1) decreases when the initial concentration increases. The concentration dependence of k_1 indicates that the photocatalytic reaction of acetone is not really first-order, even though the plot linearity of $\ln(C/C_0)$ versus t is quite well fitted. In photocatalytic studies, kinetics of degradation are generally represented by the Langmuir–Hinshelwood model. The

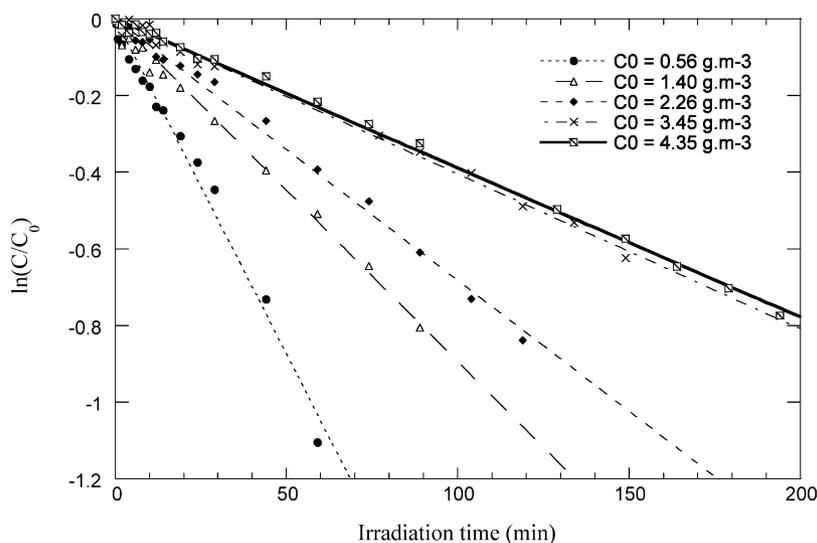


Fig. 3. The $\ln(C/C_0)$ vs. irradiation time for acetone under dry atmosphere.

Table 2

Initial reaction rates (r_0) and variation of pseudo-first-order reaction rate constant (k_1) at various initial concentrations of acetone (C_0) under dry and humid air conditions

	C_0 (g m ⁻³)	r_0 (g m ⁻³ min ⁻¹)	k_1 (min ⁻¹)	R^2
Dry air	0.56	0.0072	0.0175	0.9853
	1.40	0.0120	0.0089	0.9919
	2.26	0.0126	0.0068	0.9950
	3.45	0.0139	0.0040	0.9937
	4.35	0.0150	0.0039	0.9979
Humid air	0.51	0.0021	0.0050	0.9697
	1.52	0.0038	0.0034	0.9533
	2.57	0.0066	0.0035	0.9943
	3.27	0.0077	0.0028	0.9843
	4.69	0.0125	0.0031	0.9970

latter is defined by the following Eq. (2):

$$r_0 = \frac{kKC_0}{1 + KC_0} \quad \text{or} \quad \frac{1}{r_0} = \frac{1}{kK} \frac{1}{C_0} + \frac{1}{k} \quad (2)$$

where r_0 is the initial reaction rate (g m⁻³ min⁻¹), k the reaction rate constant (g m⁻³ min⁻¹), and K is the Langmuir adsorption constant (m³ g⁻¹). This expression is only valid at the initial stage of the reaction. During the photocatalytic process, reaction intermediates are formed and their KC terms must be included in the Langmuir–Hinshelwood rate equation. At the initial stage of the reaction, we assume that no by-products are already formed. In this study, initial reaction rates were calculated by modeling the kinetics slopes (acetone concentration C versus irradiation time t) by a third-order polynomial and by deriving it at $t = 0$ ($r_0 = (dC/dt)_{t=0}$). The results are reported in Table 2.

By drawing r_0 versus C_0 (Fig. 4) and by least squares analysis, the Langmuir–Hinshelwood reaction rate k and the Langmuir adsorption constant K can be calculated. The obtained values of Langmuir–Hinshelwood rate constant and Langmuir adsorption constant were $k = 0.02$ g m⁻³ min⁻¹ and $K = 1.39$ m³ g⁻¹, respectively ($R^2 = 0.9944$). By sub-

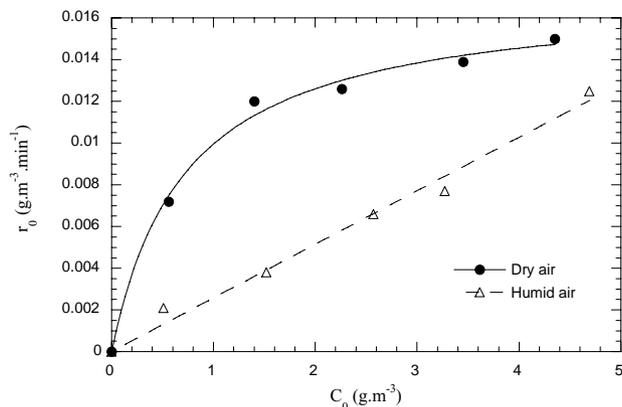


Fig. 4. The r_0 vs. C_0 for acetone in dry and humid air: effect of water vapor (markers experimental data, solid and dash lines: Langmuir–Hinshelwood model when surface reaction is rate limiting).

stituting the k and K values into Eq. (2), the analytical relationship between r_0 and C_0 is obtained. The solid line drawn in Fig. 4 represents this relationship. A good fitting of the model to the experimental data can be observed thus assuming the Langmuir–Hinshelwood nature of the photocatalytic degradation reaction mechanism. This also means that the chemical reaction is the limiting step of the process under relatively dry atmosphere.

3.1.3. Photocatalytic oxidation of acetone under humid atmosphere

A similar kinetic study was performed under humid atmosphere (RH = 30% at $T = 30$ °C) with five different initial concentrations of acetone. Values of k_1 (pseudo-first-order constants) and r_0 are given in Table 2. The first-order constants vary with acetone initial concentrations (Table 2). Thus, we seek a better representation of the photocatalytic oxidation of acetone over TiO₂-paper under humid atmosphere than the first-order reaction fitting. By representing r_0 versus C_0 (Fig. 4), it is possible to know if the Langmuir–Hinshelwood model is still valid under humid air conditions. The Langmuir–Hinshelwood model constants were not significant and errors on the calculated values were very high. A better fitting was obtained ($R^2 = 0.9933$) when adsorption was considered as the rate limiting step. In this case, the Langmuir–Hinshelwood model can be written by Eq. (3):

$$r_0 = k_{\text{ads}} C_0 \quad (3)$$

where r_0 (g m⁻³ min⁻¹) is the initial degradation rate, C_0 (g m⁻³) the initial concentration, and k_{ads} (min⁻¹) the adsorption constant. k_{ads} was calculated by least square analysis and was found equal to 0.003 min⁻¹. From these observations, it can be deduced that adsorption is really the rate limiting step in the case of photocatalytic oxidation of acetone under humid atmosphere.

The presence of water vapor has both inhibiting and activating capabilities on photocatalytic oxidation reactions of various VOC [18,24,41]. In presence of water vapor, there is a production of hydroxyl radicals due to the reaction between excited TiO₂ and H₂O (Eqs. (4) and (5)) [27,42]. Hydroxyl groups or water molecules behave as a hole trap, forming surface adsorbed hydroxyl radicals [43]. Hydroxyl radicals are very oxidative compounds that can enhance the degradation of VOC.



On the other hand, the presence of water vapor can inhibit the adsorption of pollutants onto the catalyst surface and thus lower the rate for their decomposition.

It can be observed that for every equivalent acetone initial concentration, the initial degradation rates (r_0) are always higher under dry atmosphere (Table 2). On the same way, the pseudo-first-order reaction rate constants (k_1) are always

greater under dry air conditions (Table 2). It appears that increasing the amount of water vapor has a negative effect on the photocatalytic degradation of acetone over TiO₂-paper. Comparing the curves r_0 versus C_0 in dry and humid air conditions shows that acetone degradation is strongly reduced under humid atmosphere (Fig. 4).

This result can be explained by a phenomenon of competition between acetone and H₂O molecules for the adsorption on TiO₂-paper. This is confirmed by the values of Langmuir adsorption constants obtained from isotherms plots of acetone over TiO₂-paper under dry and humid atmosphere (Table 1). We also observed that the Langmuir adsorption constants calculated from the isotherms plots and from the Langmuir–Hinshelwood model are not similar. The constant decreased when the UV-Vis lamp is switched on both under dry and humid atmosphere. This behavior was also reported by Xu and Langford [44] for the TiO₂-photocatalyzed degradation of acetophenone and by Bouzaza and Laplanche [38] through the photocatalytic degradation of toluene for two of the three tested photocatalysts. In Langmuir–Hinshelwood model, K may be viewed as a pseudo adsorption constant representing only adsorption sites involved in the photocatalytic reaction and not the total adsorption capacity of the material. This may signify that all available adsorption sites are not illuminated and do not participate to the photocatalytic degradation of the pollutant.

The adsorption of acetone onto TiO₂-paper is very low under humid atmosphere and the production of hydroxyl radicals does not allow to balance the negative effect of water vapor on acetone adsorption. Thus, on a global point of view, it can be said that water vapor greatly inhibits the photocatalytic oxidation of acetone on TiO₂-paper for initial acetone concentrations ranging from 0 to 6 g m⁻³.

3.2. 2-Butanone degradation

3.2.1. Adsorption isotherms of 2-butanone

Fig. 5 shows the adsorption isotherm plots of 2-butanone onto TiO₂-paper under dry and humid atmosphere. Circles represent experimental data and solid lines represent the Langmuir isotherm model. Parameters of the Langmuir adsorption model are summarized in Table 1. On the studied range of concentrations, 2-butanone adsorption on TiO₂-paper follows the same trend as acetone adsorption for low concentrations. 2-Butanone adsorption is also reduced under humid atmosphere but the difference between the Langmuir adsorption constant (b) in dry and humid air conditions is less important than for acetone (Table 1).

3.2.2. Photocatalytic oxidation of 2-butanone under dry atmosphere

The kinetic study of the photocatalytic oxidation of 2-butanone was performed similarly to the case of acetone. The results of pseudo-first-order reaction rate constants calculations are reported in Table 3. k_1 decreases when the initial concentration increases. This observation indi-

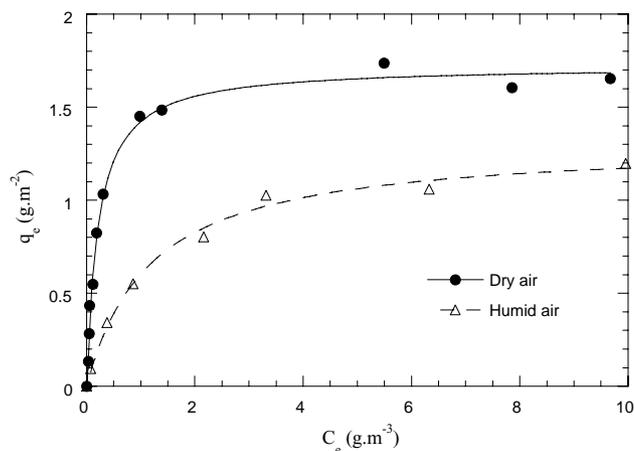


Fig. 5. Adsorption isotherm plots of 2-butanone on TiO₂-paper in dry and in humid air conditions (markers experimental data, solid and dash lines: Langmuir adsorption model).

cates that actually the photocatalytic reaction of 2-butanone is not first-order. Initial reaction rates (r_0) are given in Table 3. The obtained values of Langmuir–Hinshelwood rate constant and Langmuir adsorption constant were $k = 0.03 \text{ g m}^{-3} \text{ min}^{-1}$ and $K = 0.95 \text{ m}^3 \text{ g}^{-1}$, respectively. A good fitting of the model to the experimental data can be observed ($R^2 = 0.9873$). Thus, it can be assumed that surface reaction is the limiting step of the process under dry atmosphere.

3.2.3. Photocatalytic oxidation in humid air conditions

A similar kinetic study was achieved under humid atmosphere (RH = 30% at $T = 30^\circ\text{C}$) with five different initial concentrations of 2-butanone. Values of k_1 (pseudo-first-order constants) and r_0 are given in Table 3. The pseudo-first-order reaction rate constant varies when 2-butanone initial level changes. This means that the photocatalytic reaction of 2-butanone is not first-order. The obtained values of Langmuir–Hinshelwood rate constant and Langmuir adsorption constant by least squares analysis were $k = 0.03 \text{ g m}^{-3} \text{ min}^{-1}$ and $K = 0.48 \text{ m}^3 \text{ g}^{-1}$. A good fitting of the model to the experimental data can be observed

Table 3
Initial reaction rates (r_0) and variation of pseudo-first-order reaction rate constant (k_1) at various initial concentrations of 2-butanone (C_0) under dry and humid air conditions

	C_0 (g m ⁻³)	r_0 (g m ⁻³ min ⁻¹)	k_1 (min ⁻¹)	R^2
Dry air	0.60	0.0104	0.0308	0.9402
	1.61	0.0147	0.0138	0.9701
	2.87	0.0177	0.0069	0.9977
	4.13	0.0218	0.0053	0.9971
	5.48	0.0217	0.0040	0.9938
Humid air	0.80	0.0094	0.0136	0.9855
	2.12	0.0167	0.0097	0.9972
	3.45	0.0213	0.0073	0.9941
	4.38	0.0235	0.0063	0.9992
	6.27	0.0250	0.0052	0.9969

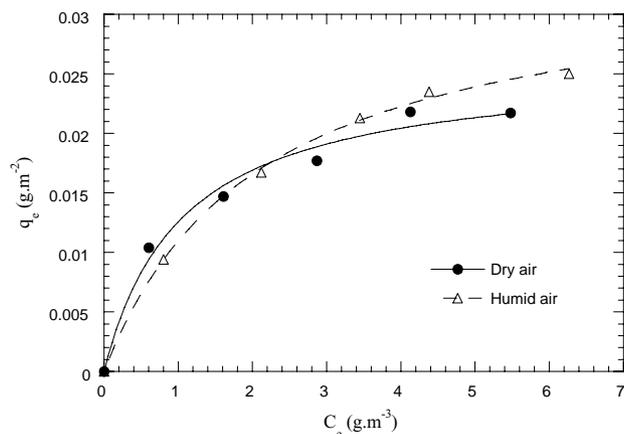


Fig. 6. The r_0 vs. C_0 for 2-butanone in dry and humid air: effect of water vapor (markers experimental data, solid line: Langmuir–Hinshelwood model when surface reaction is rate limiting).

($R^2 = 0.9993$). The chemical reaction can also be assumed to be the limiting step of the process in humid air conditions.

It can be observed that for almost every 2-butanone initial concentrations, the initial degradation rates (r_0) are higher under humid atmosphere (Table 3). This can be illustrated by comparing the curves r_0 versus C_0 under dry and humid atmospheres (Fig. 6). The values of Langmuir constants (K) obtained by fitting the Langmuir–Hinshelwood model show that 2-butanone adsorption capacity is twice lower under humid atmosphere (Table 4). This result can be explained by a phenomenon of competition between 2-butanone and H_2O molecules for the adsorption on TiO_2 -paper as shown by 2-butanone isotherm plots (Fig. 5 and Table 1). The Langmuir–Hinshelwood constants (k) are similar (Table 4). It can be concluded that water vapor does not really affect or improve 2-butanone photocatalytic oxidation on TiO_2 -containing paper for initial concentrations ranging from 0 to 6 g m^{-3} . The production of hydroxyl radicals due to the reaction between water molecules and excited TiO_2 can almost balance the negative effect of water vapor adsorption onto the photocatalyst.

3.3. Comparison between acetone and 2-butanone photocatalytic oxidation on TiO_2 -paper

The comparison can be achieved using the Langmuir–Hinshelwood model constants considering that in every cases the surface reaction is the rate limiting step. Acetone

seems to have a better affinity to be adsorbed on TiO_2 -paper than 2-butanone under dry atmosphere. Nevertheless, it appears that competition for adsorption on TiO_2 -paper with H_2O molecules is stronger for acetone than for 2-butanone. Thus, adsorption affinity on TiO_2 -paper is better for 2-butanone when experimenting under humid atmosphere.

By observing Tables 2 and 3, it appears obvious that kinetics performances are better for 2-butanone photocatalytic oxidation than for acetone using TiO_2 -containing paper as photocatalyst. The second observation is that acetone photocatalytic degradation is quite more affected by the presence of water vapor than 2-butanone. It can be concluded that several aspects should be taken into account to estimate the photocatalytic oxidation efficiency of a photocatalyst with respect to the target pollutant. Not only the pollutant adsorption affinity with the photocatalytic material is of great importance but also competitive adsorption with water vapor when experimenting under humid atmosphere. Finally, it can be said that competitive adsorption with water molecules has much more effect than adsorption affinity of pollutants with the photocatalytic material.

4. Conclusion

This study dealt with the photocatalytic oxidation of two ketones that are model pollutants of indoor air: acetone and 2-butanone. A photocatalyst composed of anatase TiO_2 deposited onto a non-woven support containing cellulose was used to perform the experiments. The objective was to compare the influence of water vapor between the two VOC. Two levels of humidity were thus tested during the experimental work. Adsorption of acetone and 2-butanone on the photocatalyst was found to be significantly affected by the presence of water vapor. Kinetic data of the photocatalytic oxidation of these ketones were analyzed using the Langmuir–Hinshelwood model at the initial stage of the reactions. In the case of acetone, water vapor greatly inhibited the photocatalytic degradation whereas it had little effect on 2-butanone oxidation. The latter was just slightly improved in humid air conditions for 2-butanone initial concentrations upper than 2 g m^{-3} . An explanation was given in term of adsorption affinity of the pollutants compared with competitive adsorption of water molecules with the ketones on the TiO_2 support. Further work consists in identifying reaction intermediates for 2-butanone degradation. Then, the kinetic law will be written using the Langmuir–Hinshelwood model on the whole reaction time including both water and reaction intermediates adsorption terms.

Table 4

Langmuir adsorption constant (K) and Langmuir–Hinshelwood rate constant (k) in dry and humid air conditions for 2-butanone

	Dry air	Humid air
k ($\text{g m}^3 \text{ min}^{-1}$)	0.03	0.03
K ($\text{m}^3 \text{ g}^{-1}$)	0.95	0.48
R^2	0.9873	0.9993

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