Enhanced Visible and Ultraviolet Light-Induced Gas-Phase Photocatalytic Activity of TiO\textsubscript{2} Thin Films Modified by Increased Amount of Acetylacetone in Precursor Solution for Spray Pyrolysis

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Abstract: TiO\textsubscript{2} thin films, modified by acetylacetone (AcacH) in solution, were deposited on glass substrate by ultrasonic spray pyrolysis and tested for photocatalytic activity in a multi-section continuous flow reactor by degradation of acetone and acetaldehyde under ultraviolet and visible light. The increase in molar ratio of AcacH in respect of titanium (IV) isopropoxide (TTIP) from 1:5 to 1:8 modified the electronic structure of the films, favoring enhanced photocatalytic activity. The photocatalytic activity was enhanced approximately twofold on the film with molar ratio 1:8 under both irradiations; the film completely oxidized 10 ppm of acetone and acetaldehyde. The photocatalytic efficacy of TiO\textsubscript{2} films in oxidation of air pollutants was three times higher compared to the industrial glass Pilkington Activ\textsuperscript{TM}. Moreover, all the synthesized films indicate antibacterial efficiency against \textit{E. coli} of over 99% under ultraviolet. TiO\textsubscript{2} film, with TTIP:AcacH molar ratio 1:8 having great possibility for its commercial use as a material for indoor air purification.

Keywords: TiO\textsubscript{2} thin film; spray pyrolysis; indoor air purification; VOC elimination; antimicrobial activity

1. Introduction

The modern lifestyle implies spending about 90% of time indoors (office, home, shops, recreation centres, etc.). Therefore, the quality of indoor air is a vital parameter for humans to sustain life [1]. Studies show that indoor air contains a variety of gases, chemicals and other substances. Common indoor air contains about 200 different gaseous components, most of them volatile organic compounds (VOCs) with the individual concentrations ≤10 ppb [2].
Concentrations of VOCs in the indoor air are up to 10 times higher than in the outdoor air since many products that are constantly used in daily life, for instance, air fresheners, cosmetics, some furniture or building materials and indoor activities like cooking release VOCs [3]. Modern homes built after 1970s are better insulated in order to obtain greater energy efficiency, which has minimized natural ventilation. According to the recommendations of the American Society of Heating, Refrigerating and Air-Conditioning Engineers (ASHREA) natural ventilation of living buildings should be able to replace 35% of the entire air by fresh outdoor air every hour. However, the value of the air exchange rate in modern buildings may be as low as 20% per hour [4]. Therefore, due to insufficient natural ventilation, air pollutants may exist in indoor air for a longer time leading to long-term exposure of humans to these chemicals. In 1983, the term “Sick Building Syndrome” was introduced to describe the situations when people experience acute health problems or feel discomfort due to staying in the building [1].

The World Health Organization (WHO) has reported that around 3.8 million people die from indoor air pollution each year [5]. Acetone and acetaldehyde are typical indoor air pollutants, the oxidative degradation pathways of which are well-studied in the literature [6–10]. In the United States, the average concentration of acetone in an office building’s indoor air is 27.1 ppb and that of acetaldehyde 4.2 ppb [2]. European Chemicals Agency (ECHA) legislation attributes acetaldehyde (EC/List no.: 200-836-8) to carcinogenic substances, which can cause genetic defects, and serious eye and respiratory irritation [11]. Moreover, in some European countries, the occupational exposure limit values for acetaldehyde have been set e.g., the limit of 8-h for workers’ exposure is 25 ppm [12].

Air-cleaning devices based on several technologies (filtration, ionising etc.) can be used to improve the poor quality of indoor air. One of the promising technologies for indoor air purification is heterogeneous photocatalytic oxidation (PCO). The main advantages of PCO are that the catalyst is relatively inexpensive and chemically inert. In the market there are several air purifiers based on the PCO principle and using TiO$_2$ nanoparticles supported on the plates as photocatalytic modules. Most of the photocatalytic air-purifiers available in the market contain an ultraviolet (UV-C) lamp and a photocatalytic module, consisting of a thick coating of TiO$_2$ nanoparticles (usually a mixture of anatase and rutile TiO$_2$ nanopowder, type P25). It has been reported that these purifiers are effective in decomposing VOCs such as formaldehyde, acetone, diethyl ether, benzene, butanol etc. and could kill bacteria and fungi in the air and on surfaces [13–15].

However, the application of these air-cleaning devices with supported TiO$_2$ nanoparticles is limited due to several factors such as further separation requirements of the powder, periodic maintenance and replacement of the photocatalyst module in the purifiers due to the low adhesion strength of nanoparticles in the layer [2,16].

To overcome these disadvantages, the nanoparticle coating with a thickness of more than couple of micrometres and specific material quantity of more than 10 mg/cm$^2$ [15] can be replaced by an economically feasible and resource-saving TiO$_2$ thin film with approximately 100 times lower material amount. In general TiO$_2$ thin films have lower photocatalytic activity compared to TiO$_2$ nanopowders. However, the deposition of transparent films onto a large surface, e.g., windows, can overcome this problem. The main advantage of TiO$_2$ thin films are transparency in the visible spectral range, good mechanical stability and adhesion [16–24], thus allowing uniform coverage of large areas and long-term stability.

TiO$_2$ coatings possess multifunctional properties when exposed to the light. In addition to the oxidation of organic pollutants, due to the super hydrophilicity the surface coated with TiO$_2$ film also has self-cleaning properties, i.e., keeping the surface free from dirt [25,26]. Moreover, hydroxyl radicals produced during the photo irradiation of TiO$_2$ can also inactivate airborne and surface-associated bacteria [27–30], fungi [28] and viruses [29]. Nakano et al. [29] used TiO$_2$ spin-coated glass to test the disinfection ability against Gram-positive bacteria (Staphylococcus aureus, Enterococcus faecalis, Streptococcus pneumonia), Gram-negative bacteria (Escherichia coli, Pseudomonas aeruginosa) and viruses (human influenza virus and feline calicivirus). They found that TiO$_2$ can be used as an effective
functional surface coating with broad-spectrum antimicrobial activity. Inactivation efficiency of infectious agents depended on the structure of their surface layers and followed this order: Gram-positive bacteria > enveloped viruses > Gram-negative bacteria > non-enveloped viruses [29].

In the last few decades, in addition to the application of TiO$_2$ in air purifiers, there has been a growing interest in the development of visible light active TiO$_2$ thin films to be used as indoor air purifying window coatings [13,31,32]. To improve the photocatalytic efficiency in visible light region TiO$_2$ films could be modified by metal doping e.g., Cu, Au, Pt, Sr and non-metal doping e.g., C, S, N [32–35] or composite material could be synthesized like TiO$_2$/SiO$_2$, TiO$_2$/WO$_3$, TiO$_2$/GO [32,33]. Several experimental and theoretical studies have reported that carbon impurities in the TiO$_2$ lattice can act as a photosensitizer, narrow the band gap, favour the formation of oxygen vacancies and create midgap states, and thereby enhance the photocatalytic activity of TiO$_2$ under UV-A and visible (VIS) light [34,36–38].

The most common methods for deposition of TiO$_2$ thin films for degradation of acetone and acetaldehyde are sputtering, sol-gel spin-coating and electrochemically assisted procedures [17–24]. Recently we have demonstrated that TiO$_2$ thin films deposited by ultrasonic spray pyrolysis with specific material quantity of 0.2 mg/cm$^2$ are effective in the decomposition of several VOCs such as acetone, acetaldehyde and heptane [6]. The interest in the fabrication of thin films by ultrasonic spray pyrolysis method is rapidly increasing due to its simplicity and the possibility to cost-effectively deposit coatings on the large surface area [6,17,26].

Chemical solution-based methods have the advantage of carbon impurities in the fabricated films, as carbon-containing precursors are used. Several strategies have been employed; to engineer the synthesis-accompanying carbon contamination in thin films fabricated by the chemical solution methods, such as varying the deposition temperature [17,39,40], post-deposition heat treatment temperature [6,17,26,38–41], amount of complexing agent [26,41–43]. The most common precursor system for solution synthesised TiO$_2$ thin films consists of titanium isopropoxide (TTIP) as a Ti-source and acetylacetone (AcacH) as a complexing agent [6,17,26,39,41–43], indicating decomposition of organic fraction in the temperature region between 100 and 550 $^\circ$C, according to the thermoanalytical studies [44,45] and the presence of carbon containing species on the film surface deposited and/or annealed at temperatures of ca 500 $^\circ$C [6,17,26,41].

A limited number of prior studies have shown that changing titanium isopropoxide (TTIP) and acetylacetone (AcacH) molar ratio in the solution from 1:0.7 to 1:2 affects photocatalytic activity of the TiO$_2$ films [42,43]. However, the first systematic study on the effect of TTIP:AcacH molar ratio on the TiO$_2$ thin films’ structural, optical properties, surface chemical composition and photocatalytic self-cleaning activity was recently published by our research group. In this study we showed that by increasing the AcacH molar ratio in the spray solution from TTIP:AcacH 1:3 to 1:20 exhibits the highest photocatalytic self-cleaning activity at optimal molar ratio of 1.8 under UV-A and VIS light [26].

The current study is a logical continuation of our previous research and provides systematic study on the effect of titanium isopropoxide and acetylacetone molar ratio in the spray solution on the photocatalytic degradation of VOCs under UV-A and VIS light, and gives insights on the effect of antibacterial activity.

The specific aims of the current study were to: (i) test the photocatalytic activity of TiO$_2$ thin films, modified by an increased molar ratio of acetylacetone to titanium isopropoxide in the spray solution, in a multi-section continuous gas flow reactor for photodegradation of acetone and acetaldehyde under ultraviolet and visible light; (ii) compare the photocatalytic efficiency of TiO$_2$ thin films with the commercial Pilkington Activ$^\text{TM}$ glass; (iii) study the effect of operating parameters such as the initial concentration of the model pollutants (acetone and acetaldehyde), air flow rate and relative humidity on the reaction kinetics; and (iv) evaluate the antimicrobial properties of the synthesized films against *Escherichia coli* according to the modified ISO 27,447 and 22,196 standards.

The results of this study demonstrate great industrial significance for the obtained TiO$_2$ thin film considering its practical application for indoor air treatment in photocatalytic degradation of
the VOCs and killing bacteria under UV-A as a photocatalytic module. Additionally, the TiO₂ thin film showed enhanced visible light photocatalytic activity, which allows the use of these films for indoor surface coatings, thus providing a photoactive alternative for the thick coatings fabricated from commercial powders.

2. Results and Discussion

2.1. Material Characterization

The detailed characterization of the morphological, optical, structural, chemical composition and wettability properties of the TiO₂ thin films with different titanium isopropoxide: acetylacetone (TTIP:AcacH) molar ratios has been reported in our previous paper [26].

The thickness of the T-1:5 film was 370 nm and that of the T-1:8 film 375 nm (Figure S1) and they were not affected by the amount of acetylacetone in precursor solution [26]. The morphology of the films surface was studied by atomic force microscopy (AFM) (Figure S2). According to AFM analysis, increasing TTIP:AcacH molar ratio from 1:4 (Figure S2a) to 1:8 (Figure S2c) in the spray solution resulted in the formation of finer grains and loss in periodic surface structure of the films. Moreover, with the increase in AcacH amount in precursor solution the variations in height across the thin film are less pronounced. Thus, an increased amount of AcacH in the spray solutions promoted the growth of TiO₂ films with more uniform surface.

According to X-ray photoelectron spectroscopy (XPS) results, the increased amount of AcacH in precursor solution resulted in higher amount of carbon adsorbed on the surface of the film (Figure S3). In our recent paper [26], we showed that the photocatalytic degradation of stearic acid layer by TiO₂ thin films rapidly increased in parallel with the increase in the AcacH molar ratio. The photodegradation rate constant changed from 0.08 to 0.24 min⁻¹ for the films with TTIP:AcacH molar ratios 1:5 and 1:8, respectively [26].

However, to better understand the enhanced photocatalytic activity of the film T-1:8, the density of states (DOS) was evaluated from the valence band (VB) XPS spectra (Figure 1b) [46]. The band gap of TiO₂ films was calculated from the Tauc plot (Figure 1a) obtained from UV-VIS total transmittance spectra. Obtained band gaps of the T-1:4, T-1:5 and T-1:8 films were 3.32, 3.33 and 3.36 eV, respectively.

![Figure 1](image_url)

**Figure 1.** (a) Tauc plot for band gap determination and (b) X-ray photoelectron spectroscopy (XPS) valence band spectra of the TiO₂ thin films with different titanium isopropoxide:acetylacetone (TTIP:AcacH) molar ratios. The inset on panel b shows zoomed Fermi level region of the TiO₂ films.

Figure 1b shows the valence band (VB) spectra of the T-1:4, T-1:5 and T-1:8 films. The T-1:4 and T-1:5 films showed VB with the edge of the maximum energy at ca. 2.65 eV, while the T-1:8 film VB top edge was at ca. 2.82 eV (Figure 1b). This means that with the increase in the AcacH amount the VB of the T-1:8 film shifted down. The down-shift in the VB top edge can be related with carbon incorporation [26,34]. Moreover, as could be seen from the plot of density of states at zero energy, which is equal to the Fermi level (Figure 1b), midgap states above VB in the band structure of the T-1:8
According to Equation (1), film with TTIP:AcacH molar ratio 1:8 can produce extra hydroxyl radicals. The potential of the T-1:8 film is more positive than the redox potential of the H$_2$O/HO$_2^-$ couple. Analogically, CB electrons reduce compounds if their redox potential is more negative than that of the adsorbed species. In the absence of suitable adsorbents, recombination of electron-hole pairs occurs [47]. Figure 2 shows that due to the downshift of VB edge the redox potential of the T-1:8 film is more positive than the redox potential of the H$_2$O/HO$_2^-$ couple [50]. According to Equation (1), film with TTIP:AcacH molar ratio 1:8 can produce extra hydroxyl radicals by oxidizing water, which increases its ability to mineralize VOCs and reduces the recombination of electron-hole pairs [47].

$$\text{H}_2\text{O} \leftrightarrow \text{HO}^- + \text{e}^- + \text{H}^+ \quad (1)$$

In our previous study we demonstrated that an increase in the amount of AcacH in precursor solution had no significant impact on structural and optical properties of the films [26]. However, increasing AcacH amount in TTIP:AcacH molar ratio from 1:4 to 1:8 influenced the surface morphology and chemical composition of the TiO$_2$ films [26]. In the current study, we showed that in addition to morphological changes, increasing the AcacH molar ratio also affected the electronic structure of the TiO$_2$ thin films. Based on the obtained results, TiO$_2$ films with TTIP:AcacH molar ratios 1:5 and 1:8 were selected for the study of their photocatalytic activity in the gas-phase since these films demonstrated the observable difference in material properties and photocatalytic degradation of stearic acid [26].

### 2.2. Gas-Phase Photocatalytic Activity of the TiO$_2$ Thin Films

#### 2.2.1. Photocatalytic Oxidation of Acetone and Acetaldehyde under Ultraviolet (UV-A) Light

In this study, acetone and acetaldehyde were chosen as model volatile organic air pollutants for the estimation of the gas-phase activity of the photocatalytic material. The application of acetone and acetaldehyde as model volatile organic air pollutants for the estimation of the gas-phase activity of photocatalytic material or performance of the reactor has been previously studied by several authors [6–10,27]. Both pollutants are hydrophilic and polar, and their oxidation occurs relatively
fast without forming long-lived intermediates. Moreover, acetaldehyde may also be one potential intermediate of acetone oxidation, depending on the degradation pathway [10].

In the current study, the oxidation of acetone and acetaldehyde was initially evaluated on the sprayed TiO$_2$ films with TTIP:AcacH molar ratios of 1:5, 1:8 in the spray solution, and commercially available Pilkington Activ$^\text{TM}$ glass applying to all five sections of the modular reactor. The obtained results for the degradation of 10 ppm of acetone and 10 ppm of acetaldehyde at air flow rate of 0.5 L/min and relative humidity (RH) 6% are presented in Figure 3. No gaseous by-products except CO$_2$ and H$_2$O were detected during the experiments. Adsorption of acetone and acetaldehyde on the films at initial concentration of 10 ppm (air flow rate 0.5 L/min and RH 6%) was studied in the dark. The difference between the reactor inlet and outlet concentrations of VOCs was not registered by Fourier transform infrared (FTIR) spectroscopy, which means the adsorption was negligible and below the detection limit of used analytical apparatus (0.5 ppm).

Figure 3 shows that T-1:8 film was on average two times more photocatalytically active than T-1:5. Complete degradation of both pollutants on the T-1:8 film surface occurred at the catalyst surface area of 240 cm$^2$, while twice the catalyst surface area (480 cm$^2$) was needed for complete degradation of 10 ppm acetaldehyde on the T-1:5 film. It was not possible, however, to achieve complete oxidation of 10 ppm of acetone on the T-1:5 film under described experimental conditions. The enhanced oxidation ability of the T-1:8 film with increase in molar ratio of AcacH in spray solution could be explained by the increase in the amount of carbon on the surface of the film [26] and changes in the electronic structure of the band gap, allowing to produce a larger number of hydroxyl radicals (Section 2.1). Dundar et al. [6] obtained the conversion of ca. 25 and 20% of 10 ppm of acetone and 10 ppm of acetaldehyde, respectively, on the sprayed TiO$_2$ film (thickness 190 nm) with TTIP:AcacH molar ratio 1:4 with catalyst surface area of 240 cm$^2$ [6]. However, on the T-1:8 film used in the current study 100% conversion of 10 ppm of acetone and 10 ppm of acetaldehyde was reached at this catalyst surface area (Figure 3).

As mentioned above, acetaldehyde is one of the oxidation by-products of acetone, thus oxidation of acetaldehyde overall should proceed faster than that of acetone. However, on the T-1:8 film for the degradation of 10 ppm of acetone and 10 ppm of acetaldehyde residence time of approximately 30 s was needed (Figure 3). The hypothesis that acetaldehyde is more easily oxidizable compound was proven in the current study since the oxidation of acetaldehyde took less time than acetone, especially on the T-1:5 film surface (Figure 3). Similar tendency has been observed by Bianchi et al. [10] on the P25 surface for the complete oxidation of 400 ppm of acetone 70 min was needed, while for complete mineralization of 400 ppm of acetaldehyde 60 min was enough [10].

TiO$_2$ films synthesized with TTIP:AcacH molar ratios 1:5 and 1:8 were generally both more active in photocatalytic degradation of 10 ppm of acetone and acetaldehyde compared to commercial...
self-cleaning Pilkington Activ\textsuperscript{TM} glass (Figure 3). Contrary to the T-1:5 and T-1:8 films obtained by the spray pyrolysis, on the commercial Pilkington Activ\textsuperscript{TM} glass the oxidation of acetone occurred slightly faster than that of acetaldehyde. On the Pilkington Activ\textsuperscript{TM} glass the change in the conversion value of acetone with the increase in residence time was very small, from 28\% to 42\% (Figure 3). Acetaldehyde conversion increased from 14\% to 38\% with residence time increasing from 15.5 to 78 s, indicating that the acetaldehyde might need more time to adsorb on the active sites of catalyst surface. This phenomenon could indicate that the oxidation process was limited by the amount of active sites on the surface of the catalyst resulting in an increase in the time needed for adsorption. Yao et al. \cite{51} have reported that adsorption of acetone and acetaldehyde on the TiO\textsubscript{2} surface occurred preferably between the carbonyl group and Ti sites. Acetaldehyde has a bare carbonyl group in the molecular structure, while in acetone structure it is surrounded by methyl groups. Therefore, acetaldehyde has stronger adsorption energy and is more stable on the surface \cite{52}. However, since acetone has higher molecular weight and lower vapour pressure compared to acetaldehyde, acetone adsorption on the active sites of the photocatalyst surface is supposed to occur faster \cite{53}. Dundar et al. \cite{6} also observed that the degradation of 5 ppm of acetone occurred faster than that of 5 ppm of acetaldehyde on the sprayed TiO\textsubscript{2} thin film, achieving 100\% conversion for acetone and ca. 80\% conversion for acetaldehyde at residence time ca. 60 s. \cite{6}.

2.2.2. Effect of Pollutant’s Initial Concentration on Its Photocatalytic Oxidation

The effect of the initial concentration of acetone on its photocatalytic oxidation on the films with TTIP:AcacH 1:5 and 1:8 was studied using three concentrations of acetone, 5, 10 and 40 ppm, at relative humidity (RH) 6\% air flow rate of 0.5 L/min (Figures 3a and 4). Moreover, the effect of acetone initial concentration on the initial reaction rate was investigated (Figure 5). Acetone was chosen as a model pollutant since acetone’s reaction rate on the T-1:5 and T-1:8 films was lower if compared to acetaldehyde.

![Figure 4. Photocatalytic oxidation of 5 ppm of acetone under UV-Air irradiation on the TiO\textsubscript{2} thin films with TTIP:AcacH molar ratios 1:5 (T-1:5), 1:8 (T-1:8) in precursor solution depending on the catalyst surface area.](image-url)
Figure 5. Initial reaction rate of acetone degradation under UV-A irradiation at different initial concentrations on the TiO$_2$ films with TTIP:AcacH molar ratios 1:5 (T-1:5), 1:8 (T-1:8) in precursor solution.

In the case of the T-1:5 film, the decrease in the concentration of acetone from 10 ppm to 5 ppm led to complete mineralization of acetone at catalyst surface area of 600 cm$^2$ (Figure 4), while at initial concentration of 10 ppm conversion was only 74% (Figure 3a). In the case of the T-1:8 film, the increase in the initial concentration of acetone from 5 ppm (Figure 4) to 10 ppm (Figure 3a) did not affect the photocatalytic oxidation; for complete oxidation the same catalyst surface area of 240 cm$^2$ was needed. However, a further increase in concentration of acetone up to 40 ppm required catalyst surface area of 360 cm$^2$ for acetone degradation on the T-1:8 film (Figure 6a).

The initial concentration of VOCs strongly affects the photocatalytic reaction kinetics [51–53]. To study the effect of the initial concentration of acetone on the reaction kinetics, the initial reaction rates ($r_0$) at initial concentrations of 5, 10 and 40 ppm at residence time of 15.6 s (catalyst surface area 120 cm$^2$) were calculated according to the Equation (2) [53].

$$r_0 = -\frac{dC}{dt}$$ (2)

Figure 5 demonstrates the dependence of initial reaction rate on the initial concentration of acetone on the films with TTIP:AcacH molar ratios of 1:5 and 1:8.
The degradation of acetone on the T-1:8 film had substantially higher initial reaction rate compared to T-1:5 whereas in case of both films the initial reaction rate depended on initial concentration of acetone (Figure 5). However, dependence of the reaction rate on concentration was not linear, indicating that the reaction rate was not diffusion-limited; oxidation reactions on the surface of thin films were supposed to be a rate-determining step. Therefore, it could be assumed that the reaction kinetics was consistent with the Langmuir–Hinshelwood model (Equation (3)) [7,23,47].

\[ r_0 = - \frac{k_r C_o}{1 + K C_o} \]  

(3)

where \( r_0 \) is initial reaction rate (ppm/s), \( C_o \) is initial concentration of acetone (ppm), \( k_r \) is reaction rate constant (ppm/s) and \( K \) is adsorption constant (1/ppm).

The linearized form of Equation (3) gives the following (Equation (4)).

\[ \frac{1}{r_0} = \frac{1}{k_r K} \frac{1}{C_o} + \frac{1}{k_r} \]  

(4)

The kinetics constants of photocatalytic oxidation reaction of acetone can be found from the plot \( 1/r_0 \) versus \( 1/C_o \), which gives a straight line (Figure S4) [54]. The kinetic parameters such as reaction rate constant and adsorption constant that were found from the Langmuir–Hinshelwood kinetic plots are listed in the Table 1.

| TTIP:AcacH in Precursor Solution | \( k_r \) ppm/s | \( K \) 1/ppm |
|----------------------------------|-----------------|--------------|
| 1:5                              | 0.728           | 0.0452       |
| 1:8                              | 2.395           | 0.0225       |

Table 1. Reaction rate constant and adsorption constant of the TiO\(_2\) films with TTIP:AcacH 1:5 and 1:8 for the degradation of acetone under UV-A irradiation.

Reaction rate constant (\( k_r \)) on the T-1:8 film was more than three times higher compared to T-1:5 (Table 1). This implies that T-1:8 film surface was very active and oxidation of pollutants occurred very fast. However, the adsorption coefficient (\( K \)) was two times lower on T-1:8 film (Table 1). Lower adsorption of acetone on the T-1:8 film was probably due to the smoother morphology of the surface (Section 2.1, Figure S2). However, due to the increased amount of active sites on the T-1:8 film, adsorption of the pollutant apparently did not limit the process.

Chang et al. [53] studied the reaction kinetics of acetone degradation in the batch annular reactor using the Langmuir–Hinshelwood model at acetone initial concentrations from 0.36 to 3.5 ppb using as a TiO\(_2\) photocatalyst P25 powder with catalyst surface area of 52 cm\(^2\). In their study, a reaction rate constant of 0.0153 ppb/s was obtained [53]. Maudhuit et al. [55] in their study of photocatalytic oxidation of 5–10 ppm of acetone in a dynamic reactor on supported P25 powder with specific quantity of material 1.6 mg/cm\(^2\) obtained the reaction rate constant of 0.110 ppm/s (air flow rate 2.5 L/min, RH 50%). It implies that design of the multi-section reactor used in the current study due to the high catalyst surface area of photocatalytically active TiO\(_2\) thin film allowed us to operate in the continuous flow regime at the concentrations measured in ppm. Due to the enhanced photocatalytic activity (Table 1), T-1:8 film was selected for further studies of the effects of operating parameters such as air flow rate and relative humidity on the photocatalytic degradation of acetone and acetaldehyde.

2.2.3. Effect of Air Flow Rate and Relative Humidity

The effect of air flow rate on the degradation of acetone and acetaldehyde at initial concentration of 40 ppm (Figure 6) and 10 ppm (Figure 7a,b) at RH 6% was studied on the film with TTIP:AcacH 1:8. The air flow rate was increased from 0.5 to 1 L/min, which reduced the residence time twofold respectively from 15.6 to 7.8 s in one section of the modular reactor.
Table 3. Initial reaction rates of acetone and acetaldehyde photocatalytic degradation at different air flow rates and relative humidity on the film with TTIP:AcacH 1:8 in precursor solution.

| Air Flow Rate, L/min | Concentration, ppm | Relative Humidity (RH), % | Acetone Initial Reaction Rate | Acetaldehyde Initial Reaction Rate |
|----------------------|--------------------|--------------------------|-------------------------------|-----------------------------------|
|                      | Concentration, ppm | Relative Humidity (RH), % | Initial Reaction Rate, ppm/s | Initial Reaction Rate, ppm/(s cm²) |
| 0.5                  | 40                 | 6                         | 1.70                          | 0.0142                            |
|                      | 10                 | 6                         | 0.74                          | 0.0061                            |
| 1                    | 40                 | 6                         | 1.59                          | 0.0132                            |
|                      | 10                 | 6                         | 0.86                          | 0.0074                            |
| 0.5                  | 10                 | 40                        | 0.20                          | 0.0016                            |
| 1                    | 10                 | 40                        | 0.37                          | 0.0031                            |

The effect of an increase in RH from 6 to 40% on the photocatalytic (UV-A light) degradation of acetone and acetaldehyde at initial concentration of 10 ppm was studied on the TiO₂ film with TTIP:AcacH molar ratio 1:8 at air flow rate 0.5 (Figure 7a,c) and 1 L/min (Figure 7b,d).

Figure 7 shows the oxidation of 40 ppm of acetone and 40 ppm of acetaldehyde at air flow rates 0.5 L/min (Figure 6a) and 1 L/min (Figure 6b) at RH 6%. The conversions of acetone and acetaldehyde at the same residence time (15.5 and 31.2 s), but doubled catalyst surface area are compared in the Table 2.

Table 2. Comparison of conversions of acetone and acetaldehyde at the residence time of 15.6 and 31.2 s at air flow rates 0.5 and 1 L/min on the film with TTIP:AcacH 1:8 in precursor solution.

| Residence Time, s | Catalyst Surface Area, cm² | Air Flow, L/min | Conversion, % |
|-------------------|-----------------------------|-----------------|---------------|
|                   |                             | 40 ppm          | 10 ppm        | 40 ppm        | 10 ppm        |
| 15.6              | 120                         | 0.5             | 46            | 67            | 75            | 68            |
|                   | 240                         | 1               | 27            | 71            | 79            | 100           |
| 31.2              | 240                         | 0.5             | 87            | 100           | 100           | 100           |
|                   | 420                         | 1               | 77            | 100           | 100           | 100           |

According to the results shown in Figure 6, an increase in air flow rate from 0.5 to 1 L/min had a negative effect on the oxidation of 40 ppm of acetone since at the same residence time (15.6 s) conversion was about 19% lower at air flow rate of 1 L/min (Table 2). The conversion of 40 ppm of acetaldehyde at the same residence time of 15.6 s is not affected by the air flow rate (Table 2). The oxidation of acetaldehyde occurred on the T:1:5 and T:1:8 films faster as discussed above (Section 2.2.2.). Therefore, it was not substantially affected by mass transfer unlike acetone oxidation. However, at initial
concentration of the pollutants of 10 ppm (Figure 7a,b) increased air flow rate had a positive effect on degradation of acetaldehyde (the conversions were 68% and 100% at the residence time of 15.6 s, at the air flow rates 0.5 and 1 L/min, respectively) and no changes in the conversion of acetone were observed (Table 2).

The increase in air flow rate resulted in the decrease in residence time of the pollutant’s molecule in the reactor and in the intensification of mass transfer of polluted air. This means that changes in fluid dynamics can either promote or inhibit the photocatalytic oxidation. However, air flow is laminar at both rates (0.5 and 1 L/min), i.e., Reynolds numbers [56] were under 40 (the calculations are not shown for the sake of brevity). In a laminar flow regime, theoretically air is moving through each reactor section layer by layer without or with minimal mixing [56]. Thus, mixing of the air takes place only after each section of the reactor due to the passing through sections connecting tubing, where air velocity drastically increases. It could be assumed that the more laminar regime at air flow rate of 0.5 L/min promoted the adsorption of acetone and, thus, the higher degree of its degradation. In the case of acetaldehyde, adsorption is supposed to be not such a pronounced prerequisite for the degradation and it was not influenced by mass transfer at higher acetaldehyde inlet concentration (40 ppm). At lower inlet concentration of acetaldehyde (10 ppm), however, the additional mixing (application of two sections of the reactor instead of one) gave its positive effect. As for the acetone at its lower inlet concentration (10 ppm), the effect of intensified mass transfer was negligible.

To estimate the effect of increased air flow rate on the reaction kinetics, the initial reaction rate \( r_0 \) was calculated according to the Equation (2). The results are presented in Table 3. At increased air flow rate the initial reaction rate of degradation of VOCs at inlet concentration of 40 ppm was 7% lower for acetone, while for acetaldehyde the initial reaction rate was 16% higher (Table 3). At an initial concentration of 10 ppm the initial reaction rate of both model pollutants was higher at air flow rate of 1 L/min; 18% and 35% for acetone and acetaldehyde, respectively (Table 3). These results demonstrate that differences in air flow regime affected the reaction kinetics; the effect was more pronounced at lower inlet concentrations of pollutants and depended on the type of pollutant. The differences in the character of oxidation of pollutants could be easily monitored using a continuous multi-section reactor.

**Table 3. Initial reaction rates of acetone and acetaldehyde photocatalytic degradation at different air flow rates and relative humidity on the film with TTIP:AcacH 1:8 in precursor solution.**

| Air Flow Rate, L/min | Concentration, ppm | Relative Humidity (RH), % | Acetone | Acetaldehyde |
|----------------------|--------------------|---------------------------|---------|--------------|
|                      |                    |                           | Initial Reaction Rate | Initial Reaction Rate |
|                      |                    |                           | ppm/s    | ppm/(s cm²)  | ppm/s     | ppm/(s cm²) |
| 0.5                  | 40                 | 6                         | 1.70     | 0.0142       | 2.01      | 0.0167      |
| 1                    | 40                 | 6                         | 1.59     | 0.0132       | 2.38      | 0.0199      |
| 0.5                  | 10                 | 6                         | 0.74     | 0.0061       | 0.66      | 0.0055      |
| 1                    | 10                 | 6                         | 0.86     | 0.0074       | 1.17      | 0.0084      |
| 0.5                  | 10                 | 40                        | 0.20     | 0.0016       | 0.60      | 0.0050      |
| 1                    | 10                 | 40                        | 0.37     | 0.0031       | 0.72      | 0.0060      |

Liang et al. [23] studied the effect of air flow rate on the oxidation of acetone in a cylindrical reactor where sol-gel-synthesized 0.2 mm thick anatase TiO₂ film attached to glass spring was used as a catalyst. They showed that for 2445 ppm of acetone the intensification of mass transfer promoted the oxidation despite the decrease in residence time. The efficiency of photocatalytic oxidation increased from 18 to 78% with the increase in air flow rate from 1 to 3 L/min; however, a further increase in air flow up to 9 L/min resulted in drastic drop in photocatalytic efficiency to approximately 5% [23], which confirms that ascertaining the optimal air flow rate is an important step in technology development.

The effect of an increase in RH from 6 to 40% on the photocatalytic (UV-A light) degradation of acetone and acetaldehyde at initial concentration of 10 ppm was studied on the TiO₂ film with TTIP:AcacH 1:8 at air flow rate 0.5 (Figure 7a,c) and 1 L/min (Figure 7b,d).
Complete oxidation of 10 ppm of acetone and acetaldehyde at an air flow rate of 0.5 L/min was achieved at a catalyst surface area of 240 cm², when relative humidity was 6% (Figure 7a). At relative humidity of 40%, for the complete degradation of acetone the catalyst surface area was increased two times (480 cm²), while for acetaldehyde it remained the same at 240 cm² (Figure 7c). Table 3 demonstrates, that at lower air flow rate (0.5 L/min) water molecules inhibited the degradation of acetone, the initial reaction rate was 74% lower at RH 40%. For 10 ppm of acetaldehyde at lower air flow rate, an increased amount of water molecules had no specific effect on photocatalytic degradation of pollutant. However, when the air flow rate of 1 L/min was used the initial reaction rate was decreased for both model pollutants at RH 40%.

The increased amount of water molecules can influence the performance of the photocatalytic oxidation process in different ways; this effect strongly depends on the water vapour concentration and the type of pollutant. The photocatalytic reaction rate can be enhanced since water molecules act as hole traps and form hydroxyl radicals participating in the oxidation of pollutants. On the other hand, water molecules can inhibit the adsorption of some pollutants on the surface of the catalyst, which may lead to a decrease in the degradation efficiency [6,26,47]. In this study, the increase in the RH from 6 to 40% deteriorated the performance of photocatalytic oxidation of VOCs despite the probable formation of higher number of hydroxyl radicals. Supposedly, water adsorbed on the active sites of TiO₂ thin films and inhibited the adsorption of the pollutants, thus the prolonged residence time may contribute to complete degradation of VOCs at higher water vapour content.

The same observations on the negative effects of an increased water vapour amount on oxidation of acetone and acetaldehyde have been reported by other authors [56–58]. Kim et al. [57] showed that on dip-coated TiO₂ thin film with thickness of 65 nm the increase in the amount of water vapour from 0 to 0.766 mol/m³ decreased the photodegradation rate of 274 ppm of acetone from 0.71 ppm/s to 0.21 ppm/s [57]. Seo et al. [58] studied the degradation of acetaldehyde at different RH on the 7 µm thick P25 layer and observed the decrease of 16% in the photodegradation rate with an increase in RH from 0% to 33.6% [58].

2.2.4. Photocatalytic Oxidation of Acetone and Acetaldehyde under Visible Light

Sprayed TiO₂ thin films were tested for photocatalytic oxidation of 10 ppm of acetone and 10 ppm of acetaldehyde under VIS light (Figure 8). The effect of air flow rate and relative humidity on the photocatalytic oxidation of acetone and acetaldehyde under VIS light was also studied. (Figure 8). Figure 8a demonstrates that TiO₂ film with molar ratio 1:8 was capable of oxidizing 10 ppm of acetaldehyde and 10 ppm of acetone under VIS light at catalyst surface area of 360 and 480 cm², respectively (air flow rate 0.5 L/min, RH 6%). For the comparison under UV-A light the photocatalytic activity of the films was substantially higher; both model compounds were fully degraded at a catalyst surface area of 240 cm² on the T-1:8 film (Section 2.2.1, Figure 3). The initial reaction rates on the T-1:8 film at air flow rate of 0.5 L/min and RH 6% under VIS were 0.35 ppm/s for 10 ppm of acetone and 0.52 ppm/s for 10 ppm of acetaldehyde which is, respectively, 53 and 21% lower compared to results obtained under UV-A (Table 3).
The oxidation of pollutants under VIS light needed more residence time in the reactor since the photocatalytic activity of the film was lower compared to UV-A.

**Figure 8.** Effect of air flow rate and relative humidity (RH) on photocatalytic oxidation of 10 ppm acetone and 10 ppm of acetaldehyde under visible (VIS) light on the films with TTIP:AcacH molar ratio 1:8 in precursor solution at RH 6% air flow rates (a) 0.5 and (b) 1 L/min and at RH 40% air flow rates (c) 0.5 and (d) 1 L/min depending on catalyst surface area.

The photocatalytic activity of the film with TTIP:AcacH molar ratio 1:5 under VIS light was very low, ca. 20% conversion of pollutants was achieved at residence time of 78 s (Figure S5). However, the increase in the content of organic matter by changing the AcacH molar ratio in precursor solution enhanced the photocatalytic activity of the T-1:8 film (Figure 8a). Previous studies have clearly demonstrated that carbon incorporation in TiO$_2$ photocatalyst enhanced the photocatalytic activity for the degradation of stearic acid, 4-clorfenol, paroxon and methylene blue under VIS light [26,34,56–58], while the current study showed also profound improvement in the photocatalytic oxidation of VOCs.

The increase in the air flow rate from 0.5 (Figure 8a) to 1 L/min (Figure 8b) under VIS light inhibited the degradation of model pollutants at lower residence time (15.5 s) and promoted the degradation at higher residence time (31.2 s). In Figure 8a,b, at the same residence time of 15.6 s (air flow rates 0.5 and 1 L/min, catalyst surface areas 120 and 240 cm$^2$, respectively) the conversion was higher at lower air flow rate of 0.5 L/min (catalyst surface area 120 cm$^2$ on the Figure 8a). However, at residence time of 31.2 s (air flow rates 0.5 and 1 L/min, catalyst surface areas 240 and 480 cm$^2$, respectively) conversion was higher at an air flow rate of 1 L/min (catalyst surface area 480 cm$^2$ on the Figure 8b). Increased mass transfer at residence time 15.6 s had negative effect on the photocatalytic oxidation. However, at the residence time 31.2 s additional mixings (application of four sections of reactor instead of two) had a positive effect on the degradation of model pollutants. The oxidation of pollutants under VIS light needed more residence time in the reactor since the photocatalytic activity of the film was lower compared to UV-A.

The increase in RH from 6 to 40% strongly inhibited the degradation of acetone and acetaldehyde under VIS light (Figure 8a,c). However, if under UV-A at a lower air flow rate (0.5 L/min) the effect of water vapour on photocatalytic oxidation of acetaldehyde was almost imperceptible (Section 2.2.3,
A similar tendency as under UV-A irradiation was observed, acetone oxidation is more affected by the increase in air RH compared to acetaldehyde.

2.2.5. Reusability of the Film

The reusability of the photocatalytic materials is an important factor to consider since it shows the practical application of the material for air purification from VOCs [28]. In order to estimate the lifetime of the sprayed TiO$_2$ thin film the reusability of the film with TTIP:AcacH molar ratio 1:8 under UV-A irradiation was studied. No deactivation of the photocatalyst was observed after more than three months of daily work with a short regeneration (approximately 30 min) of the TiO$_2$ films with UV-A light after each experimental run. Moreover, a long-term experiment on the photocatalytic oxidation of 40 ppm of acetone on the T-1:8 film under UV-A irradiation was carried out (Figure 9). The results confirmed that the film had extreme stability and high photoactivity for at least 120 min of continuous use.

![Fourier transform infrared (FTIR) spectra of characteristic acetone C–CO–C stretching at different times of experimental run under UV-A irradiation on the TiO$_2$ film with TTIP:AcacH molar ratio 1:8 in precursor solution.](image)

Figure 9. Fourier transform infrared (FTIR) spectra of characteristic acetone C–CO–C stretching at different times of experimental run under UV-A irradiation on the TiO$_2$ film with TTIP:AcacH molar ratio 1:8 in precursor solution.

Some experiments with acetaldehyde on the film with TTIP:AcacH 1:8 were repeated after at least one month of daily experiments to check the repeatability of the results. The average difference in the initial reaction rates between I and II experimental runs was 3.0% and did not exceed 5.3% for an individual series of experiments (Figure 10).

![The repeatability of initial reaction rate values for some series of experiments on acetaldehyde oxidation under UV-A irradiation on the TiO$_2$ film with TTIP:AcacH molar ratio 1:8 in precursor solution.](image)

Figure 10. The repeatability of initial reaction rate values for some series of experiments on acetaldehyde oxidation under UV-A irradiation on the TiO$_2$ film with TTIP:AcacH molar ratio 1:8 in precursor solution.
Thus, an applied 30-min regeneration of the film with UV-A light allows continuous long-term application of this type of TiO₂ thin films for the degradation of acetone and acetaldehyde without any loss in films’ photocatalytic activity. The study on the optimal time for the regeneration of the film with TTIP:AcacH 1:8 will be of great interest in the future; however, this was not under the scope of present research.

2.3. Antibacterial Activity

An antibacterial test was performed in the liquid phase since drying of the system leads to inactivation of the most used laboratory strains of bacteria and renders test results inconclusive. The well-established protocol was used; it allows us to compare the results with preceding literature and commercial products [59]. Antibacterial activity of the photocatalytic TiO₂ films with TTIP:AcacH molar ratios 1:4, 1:5 and 1:8 towards the Gram-negative model organism *Escherichia coli* MG1655 is shown in Figure 11.

All the TiO₂ films irrespective of TTIP:AcacH molar ratios demonstrated strong antibacterial activity of over 99% reduction in viable counts compared to the control surface during 60 min exposure with UV-A illumination (p < 0.0001). Despite very small statistically significant difference (16% reduction in viable count compared to the control in case of T-1:8 film, P = 0.04) no biologically relevant antimicrobial activity was observed in dark conditions. The antibacterial activity was not enhanced with the increase in AcacH amount. Less variable results on the T-1:8 film under UV-A illumination could partly be obtained due to the superior surface morphology. Indeed, the surface of the film with TTIP:AcacH 1:8 is smoother and more uniform (Section 2.1, Figure S3).

Many authors have reported that the reactive oxygen species (ROS) generated by TiO₂ have antibacterial activity. However, it should be mentioned that the bactericidal mechanism is more complex compared to VOCs oxidation since bacteria are complex unicellular organisms separated from the surrounding environment by a membrane and cell wall [60,61]. Thus, the mechanism of degradation of bacterial cells includes, first, damage to the cell wall, peroxidation of membrane lipids and further leakage of the cytoplasm due to the membrane damage [16]. Our results are comparable with those obtained by Kim and Kwak [62], who obtained 99% degradation of 1 × 10⁶ cells/mL *E. coli* for the mesoporous P25 films after 60 min of UV-A irradiation [62].
All TiO$_2$ thin films obtained in the current study indicate antibacterial activity, in addition to gas-phase photocatalytic oxidation of VOCs. However, to compare the results of the film’s gas-phase photocatalytic efficiency with antibacterial activity further tests with airborne microorganisms are needed, which is of great interest and will be under the scope of future studies.

3. Materials and Methods

3.1. Preparation and Characterization of TiO$_2$ Thin Films

Anatase phase TiO$_2$ thin films with thickness of ca. 400 nm were deposited on borosilicate glass substrate at temperature of 350 °C by ultrasonic spray pyrolysis technique. The details of the film preparation have been published elsewhere [26]. The as-deposited films were annealed for one hour at 500 °C in air. Titanium (IV) isopropoxide (TTIP): acetylacetone (AcacH) molar ratios 1:4, 1:5 and 1:8 were used for precursor solution preparation, the samples obtained were further designated T-1:4, T-1:5 and T-1:8, respectively. The concentration of TTIP was 0.2 M.

The band gap of TiO$_2$ thin films was calculated from the Tauc plot using total transmittance spectra measured with a Jasco V-670 UV-VIS-NIR (near infrared) spectrophotometer (Jasco, Tokyo, Japan) equipped with an integrating sphere in the spectral range 250–1500 nm. X-ray photoelectron spectroscopy (XPS) with a Kratos Analytical AXIS ULTRA DLD spectrometer (Kratos Analytical, Manchester, England) in conjunction with a 165-mm hemispherical electron energy analyzer and delay-line detector was used to analyse the location of the valence band.

3.2. Evaluation of Gas-Phase Photocatalytic Activity of the TiO$_2$ Thin Films

Photocatalytic oxidation of acetone and acetaldehyde (both Sigma-Aldrich, ≥ 99.5% purity) over TiO$_2$ thin films was studied in a continuous multi-section plug flow reactor. A detailed description of the set up for photocatalytic experiments was published elsewhere [63]. The reactor consists of five sections with the volume of 130 mL each. Four pieces of TiO$_2$ thin film with dimensions 4 cm × 7.5 cm were placed inside each section, giving the catalyst surface area 120 cm$^2$ per section and 600 cm$^2$ for five sections. UV Philips Actinic BL 15 W, irradiance 3.5 mW/cm$^2$ with reflector (integrated in the range of 180–400 nm, with maximum emission at 365 nm, UV-B/UV-A ratio <0.2%) lamps were used as an UV-A irradiation source and VIS Philips TL-D 15 W, irradiance 3.3 mW/cm$^2$ with reflector (integrated in the range of 180–700 nm, UV/UV-VIS ratio <5%) lamps as VIS irradiation source over each section of the reactor with the distance of 6 cm. The construction of this modular reactor allows an increase in the residence time in the reactor by increasing the catalyst surface area without changing the mass transfer in the reactor. Polluted (spiked with acetone and acetaldehyde) air was prepared in a 50 L tank using regular ambient air. Two air flow rates 0.5 and 1 L/min were used during the experiments, which yielded the residence time in the reactor 15.6 and 7.8 s per section, respectively. The air flow rate was measured by two gas flow controllers, one for measuring the diluent and one for the polluted gas flow rates. Gas humidifier was used to change the air humidity. INTERSPEC 200-X FTIR infrared spectrometer (Interspectrum OÜ, Tõravere, Estonia) with the 8 m gas cell (Specac) was used for measuring the concentration of VOCs. Spectra were acquired in the absorbance mode, with the number of scans 5 and resolution 1 cm$^{-1}$. The spectra of filtered and dried ambient air were used as a reference. The characteristic C–C stretching of acetone was measured at the IR bands from 1270 to 1240 cm$^{-1}$ [64] and C–H aldehyde stretching of acetaldehyde at the IR bands from 2900 to 2600 cm$^{-1}$ [65] and were quantified with the limit of detection of about 0.5 ppm and the limit of quantification of 1.0 ppm. All spectra were measured at least twice and the difference between the experiments did not exceed 5%. The air spectra were acquired using an Interspec version 3.40 Pro (Interspectrum OÜ, Estonia, 2012) and processed by the Essential FTIR software (Version 3.50.075, Operant LLC, Madison, WI, USA, 2016).
3.3. Study of Antibacterial Activity of the TiO₂ Thin Films

The surfaces of TiO₂ thin films were pre-treated by rinsing with 70% ethanol and 3 mW/cm² UV-A irradiation (24 h) in aseptic conditions. Antibacterial testing was carried out using an in-house protocol based on modified ISO 27,447 and ISO 22,196 protocols [59]. Bacterial suspension was prepared in 500-fold diluted nutrient broth (NB: 3 g/L meat extract, 10 g/L peptone, 5 g/L NaCl in deionized water), optimized to optical density (600 nm) of 0.01 resulting in 5 × 10⁴ cells per cm². To determine the antibacterial properties of test surfaces, 15 μL of bacterial suspension was applied to test surface and covered with 20 × 20 × 0.05 mm polyethylene film to attain an even, thin coverage of bacterial suspension with good contact between bacterial cells and the surface and even UV-A exposure. Samples were kept either in the dark or exposed to 0.26–0.33 mW/cm² UV-A irradiation measured in the 315–400 nm spectral range. Surfaces with bacterial suspension were incubated in a humid environment on a bent glass U-rod over sterile wet filter paper covered by Petri dish cover in dark conditions or 1.1 mm thick UV-A-transmissive borosilicate moisture preservation glass under UV-A illumination. UV-A intensity was measured at a test surface height with a light meter detector covered by both polyethylene film and borosilicate moisture preservation glass. Media, solutions and glass rods were autoclaved at 121 °C for 15 min prior to each experiment. Polyethylene cover films and control surfaces were rinsed with 70% ethanol and air-dried under UV-C irradiation. After exposure, each sample was washed with 2 mL of toxicity neutralizing soybean casein digest broth with lecithin and polysorbate medium (SCDLP: 17 g/L casein peptone, 3 g/L soybean peptone, 5 g/L sodium chloride, 2.5 g/L disodium hydrogen phosphate, 2.5 g/L glucose, 1 g/L lecithin and 7 g/L polysorbate 80 in deionized water) by pipetting, serially diluted in phosphate buffered physiological saline (PBS) and drop-plated for counting. Nutrient agar (NA: 5 g/L meat extract, 10 g/L peptone, 5 g/L sodium chloride, 15 g/L agar powder in deionized water) was used for plating and colony forming units were counted after 24 h incubation at 30 °C. Statistical analysis to detect statistically significant differences in viable counts was performed by one-way analysis of variance (ANOVA) followed by Tukey’s HSD (honestly significant difference) using the program GraphPad Prism version 8.3.0 (GraphPad Software, LLC, San Diego, CA, USA, 2019).

4. Conclusions

TiO₂ thin films with an increased amount of AcacH in precursor solution were deposited on borosilicate glass substrate by the ultrasonic spray pyrolysis technique. The increased molar ratio of AcacH changed the position of valence band, leading to the higher production of hydroxyl radicals on the catalyst surface and thus enhanced the photocatalytic activity of the TiO₂ thin films under ultraviolet (UV-A) and visible (VIS) lights. Indeed, the efficiency of photocatalytic oxidation of 10 ppm of acetone and 10 ppm of acetaldehyde on the film T-1:8 was about two times higher compared to film T-1:5 under UV-A and VIS irradiation. The reaction kinetics was studied using the Langmuir–Hinshelwood model. The initial reaction rate of acetone oxidation increased as expected, with an increase in its concentration on both films. However, the reaction rate constant on film T-1:8 was more than three times higher compared to T-1:5. The increase in air flow rate had different effects on the oxidation of pollutants depending on their initial concentration. Higher air humidity had negative effect on the degradation of acetone and acetaldehyde, but for acetaldehyde the effect was less pronounced, especially under UV-A irradiation. TiO₂ thin films demonstrated strong antibacterial activity towards Gram-negative E. coli under UV-A irradiation irrespective of TTIP:AcacH molar ratio in precursor solution. Thus, the results of this study demonstrate that TiO₂ films with TTIP:AcacH molar ratio 1:8 could be successfully applied for indoor air purification in photocatalytic air cleaners instead of powder modules since their efficiency under UV-A is substantially higher than that of commercial Pilkington Activ™ glass and comparable with thick coatings of P25 nanopowder used in the literature. The results of visible light photocatalytic activity showed that film deposited on a large surface area could be applied as an indoor air purifying coating. Moreover, the antimicrobial properties including the
antiviral properties need further investigation under visible light as obtained films may have the potential for the purification of microbial-polluted indoor air.

**Supplementary Materials:** The following are available online at [http://www.mdpi.com/2073-4344/10/9/1011/s1](http://www.mdpi.com/2073-4344/10/9/1011/s1).

- Figure S1: Cross-sectional scanning electron microscopy (SEM) image of TiO$_2$ thin film on borosilicate glass substrate at TTIP:AcacH molar ratio 1:8 (T-1:8), Figure S2: Atomic force microscope (AFM) images of the TiO$_2$ films (a) T-1:4, (b) T-1:5 and (c) T-1:6, Figure S3: X-ray photoelectron spectroscopy (XPS) spectra of Cls core level for (a) 1:5 and (b) 1:8 TTIP:AcacH molar ratios in precursor solution for TiO$_2$ thin films, Figure S4: Langmuir-Hinshelwood kinetic plot for the determination of acetone degradation reaction rate constant and adsorption constants on TiO$_2$ films with TTIP:AcacH molar ratios (a) 1:5 and (b) 1:8 in precursor solution, Figure S5: Photocatalytic oxidation of 10 ppm of acetone and 10 ppm of acetaldehyde under VIS light on the T-1:5 film depending on the catalyst surface area.

**Author Contributions:** J.S.: Conceptualization, Investigation, Formal analysis, Writing—Original Draft, Visualization. A.M.: Investigation, Formal analysis. M.K. (Malle Krunks): Formal analysis, Funding acquisition, Writing—Review and Editing. M.R.: Antibacterial activity Investigation, Formal analysis, Validation, Writing—Review and Editing. A.K.: Writing—Review & Editing. M.D.: XPS Investigation, Formal analysis. M.K. (Marina Krichevskaya): Conceptualization, Methodology, Writing—Review and Editing, Supervision. I.O.A.: Conceptualization, Methodology, Writing—Review and Editing, Supervision, Resources, Funding acquisition. All authors have read and agreed to the published version of the manuscript.

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