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Photocatalytic Oxidation of H₂S in Gas Phase Over TiO₂-coated Glass Fiber Filter

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Filter

Hydrogen sulfide (H_2S) is a malodorous, toxic and corrosive compound emitted into the atmosphere by anthropogenic and natural sources. Due to the need to protect the environment and population from possible impacts of this pollutant, an annular reactor packed with filter mats fabricated of glass fiber was evaluated for photocatalytic oxidation of H₂S in gas phase. TiO₂ thin films coated on the glass fibers were characterized structurally and morphologically by field emission gun scanning electron microscopy (FEG-SEM), scanning electron microscopy (SEM) coupled with energydispersive x-ray spectroscopy (EDS) and x-ray diffractometry (XRD). Flow rate and H₂S inlet concentration were evaluated to determine the performance of the reactor. Photocatalytic efficiencies of H₂S removal up to 99% were achieved for the experiments conducted with volumetric flow rate of 25 1.h⁻¹ (residence time of 121 s) and H₂S inlet concentration from 12 to 14 ppm_v. The long-term experiment presented H₂S removal of 89% maintained for 16 h. After 28 h of continous use, H₂S degradation was observed at 64%, which suggests that the photocatalyst was finally losing activity due to deactivation. Moreover, the kinetics of the photocatalytic oxidation of H_2S according to Langmuir-Hinshelwood (L-H) approach along with the mass balance of a plug-flow reactor was modeled. The reaction constant (k) was calculated at approximately 10.5 μ mol.m³ s⁻¹ and the adsorption constant (K) of approximately $5,263 \text{ m}^{-3}$.mol with linearity (\mathbb{R}^2) of 0.98.

Keywords: photocatalysis; hydrogen sulfide; TiO2; photoreactor, glass fiber.

1. Introduction

Odour exposure that result from anthropic activities may cause an adverse effect on health status, social and individual life. This exposure is frequently classified as airborne pollutants and, hence, subject to control and regulation [1]. Basically, odours can be defined as a sensory response to inhalation of specific chemical species present in the air, including sulfur compounds (e.g., sulfides mercaptans), nitrogen compounds (e.g., ammonia, amines) and volatile organic compounds (VOCs) (e.g., esters, acids, aldehydes, ketones, alcohols) [2]. Among these substances, hydrogen sulfide (H₂S) stands out for being a colorless, flammable. toxic, corrosive gas with a characteristic rotten egg smell [3, 4, 5]. Several H₂S odour threshold values are reported in the literature, ranging from 0.0005 - 0.3 ppm_v [6]. However, typical values are in the range of 0.4 - 0.5 ppb_v [2, 4, 7, 8]. The emission of H₂S can occur through natural processes (e.g., volcanoes, hot springs and wetlands) and anthropogenic sources, such as oil and gas extraction, petroleum refining, coke ovens, kraft paper mills, waste water treatment plants, intensive pig farming, fertilizing soil with manure, tanneries, sugar manufacturing, leather production and landfill disposal systems [4, 5, 6, 9, 10, 11]. Indeed, there are more than 70 occupation types involving contact with H₂S with fatal episodes due to the contact with the pollutant. Therefore, H₂S removal is relevant not only for public concern over human health risky and nuisance (offensive odour), however for environmental reasons (acid rain precursor) and maintenance issues (corrosion in equipments). Common technologies applied for H₂S control include prevention, masking, biofiltration, bioscrubbing, chemical scrubbing, combustion and adsorption processes. Although many of these methods have already been applied in real-scale facilities, they lack long-term stability, require handling of chemicals, or high-energy consumption [9, 10, 12].

Photocatalytic oxidation (PCO) represents the newest generation of proactive air treatment technology that offers distinct benefits: very suitable for trace pollutant

concentrations removal; titanium dioxide (TiO₂), the most commonly used photocatalyst, is a non-toxic compound, chemically and biologically inert in its natural form with relatively low cost and high availability [13, 14, 15, 16, 17, 18, 19]. In the mean time, studies have demonstrated toxicological effects of TiO₂ nanoparticles in various organisms (e.g., blue mussel, microbial communities, benthic organisms, zebrafish embryos, cladocerans, rotifers, algae) and even in tests with human blood [20, 21, 22, 23, 24, 25, 26]. Since Fujishima and Honda [27] described the potential of TiO₂ electrode to split water into hydrogen and oxygen in a photoelectrochemical cell, the interest in heterogeneous photocatalysis is continuously increasing, especially in environmental and energy production applications [28, 29]. TiO2based photocatalytic technology for air treatment is an attractive and efficient route when compared to other conventional techniques, since PCO generally presents mild reaction conditions, harmless by-products, low-cost implementation and energy consumption. In addition, photocatalytic semiconductors are able to mineralize the pollutants, instead of phase transfer as, for instance, adsorption with activated carbon [30, 31]. However, H₂S PCO studies [9, 10, 12, 32, 33, 34, 35, 36, 37, 38, 39, 40] are scarce and rarely investigated compared to VOCs degradation.

There are Different formulations are available in the literature for modelling photocatalytic reactors. Especially annular photocatalytic reactors, operating without recirculation, can be modelled with the simple model assuming ideal flow and steady state conditions. Basically, this is possible using the one – dimensional (1D) heterogeneous model [41]. When the corresponding model assumptions are valid and the proper semiempirical correlations exist, 1D models have shown accurate predictions in simple reaction systems [42]. Kinetic modelling, that describe the photocatalytic degradation of pollutants, should consider the adsorption-desorption and chemical kinetics. In this regard, Langmuir-Hinshelwood (L-H) is the most used modeling approach for liquid or gaseous heterogeneous photocatalytic processes [18, 43, 44, 45, 46]. Meanwhile, only few studies [37, 47] applied the L-H theory to the photocatalytic degradation of H₂S in the gas phase.

This paper reports an experimental study of photocatalytic oxidation of H₂S in the gas phase using an annular photoreactor packed with filter mats manufactured of glass fiber. Thin films were coated on the support material and characterized to visualize the surface morphology, thickness, elemental composition and to determine the phase composition and the crystallite size of TiO₂ P 25 nanoparticles. The performance of the photoreactor was evaluated with respect to H₂S inlet concentration and flow rate. Long-term use of the photocatalyst was also conducted to assess the deactivation time. Furthermore, kinetics of the photocatalytic degradation of H₂S was modeled according to L-H approach together with a photoreactor operating under plug-flow hydraulic regime.

2. Experimental

2.1. Formation of TiO₂ thin films on glass fiber filters

To immobilize TiO₂ thin films on filter mats fabricated of glass fiber (Linter, FV-25, grammage of 300 g.m⁻², dimensions of 35 cm by 20 cm) a simple and effective immersion method was applied. First, the cleaning of the support material was performed. This is a fundamental step for the formation of thin films. If the cleaning procedure is not efficacious, it is possible that the deposition of the thin film is not uniform over the surface of the substrate, thereby forming a discontinuous film. For this purpose, the glass fiber filters were sequentially sonicated in a solution of HCl 0.5 M and NaOH 1 M, during 30 min in an ultrasonic bath (Quimis, Q335D) and rinsed in deionized water between the applications of solutions [48, 49, 50]. Following, 4 g of TiO₂ P 25 (Evonik Industries, Aeroxide®) was added to 1 L of deionized water [48, 50, 51]. TiO₂ P 25 powder was used as received, without any pretreatment. The pH of the suspension was adjusted to approximately 3 using HCl [50] to

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avoid aggregation and sedimentation of TiO₂ nanoparticles. To ensure homogeneity and satisfactory dispersion of the photocatalyst, the suspension was stirred vigorously for 20 min in a magnetic stirrer (FiSatom, 752). Subsequently, glass fiber filters were immersed into the aqueous suspension at room temperature (20 °C) with diving time of 30 min to be coated with TiO₂ P 25. After deposition by immersion, glass fiber filters were left to dry in air over a period of 24 h and heat-treated in a muffle furnace (Quimis, Q318S24) at 120 °C (++7°C, heating ramp of 5.5 °C.min⁻¹) for 1 h [52] to improve fixation of the photocatalyst on the media [53]. Immersion and heat treatment can be repeated until the proper formation of the thin film [54]. The coating procedure was performed 3 times. TiO₂ loading of the glass fiber filters was measured by weighing samples before and after coating, and found to be 10.33 \pm 1.23 g.m⁻², corresponding to a mass of 0.031 \pm 0.0037 g of photocatalyst in the packed bed (i.e., per glass fiber filter). The combination of different approaches of thin films formation provided a facile, economical and improved approach of TiO₂ thin films coating on glass fiber filters.

2.2. Characterization techniques

Field emission gun scanning electron microscopy (FEG-SEM) and scanning electron microscopy (SEM) coupled with energy-dispersive x-ray spectroscopy (EDS) were performed by a JEOL JSM-6701F and a Phillips XL30, respectively. An ultra-thin coating of electrically-conducting metal of gold ions was applied onto non-conducting fiber glass specimens using a sputter coater (Baltec, SCD 005). Finally, samples were mounted onto stainless-steel holders with a double-sided carbon tape for analysis.

X-ray diffraction (XRD) analyses were conducted using X-ray diffractometer (Philips, X'Pert) operating in reflection mode with Cu-K α radiation (λ = 1.54056 Å, 40 kV, 30 mA) in

the range of 2θ from 3° to 118° at a scanning speed of 0.05° per second. The intensity of the X-ray diffraction peaks of TiO₂ coated glass fiber is too weak to identify crystalline phases [52, 55]. Then, to perform XRD analyses TiO₂ P 25 powder as received (Sample 1) and TiO₂ P 25 powder subjected to the heat treatment described in Section 2.1 (Sample 2) were used. The mean crystallite size of the photocatalysts were determined from XRD line broadening measurements using the Scherrer's equation [56]:

 $D = K\lambda / \beta \cos\theta$



Where, D is the particle size, K is the particle shape factor (assumed as sphere = 0.90), λ is the X-ray radiation wavelength, θ is the diffraction angle and β is the line width at half maximum of diffraction peak height, in radians.

2.3. Photocatalytic reactor

A tubular reactor of annular type built in borosilicate glass with inner diameter of 6 cm and 36 cm in length was designed and manufactured for the photocatalytic tests. The reactor has gas inlet and outlet of 8 mm diameter with radial introduction of the reactant mixture and polypropylene removable covers at the extremities to introduce the packing material. Illumination was provided by adding a UV light lamp (G-Light, T8, 15W) with outer diameter of 2.5 cm on the central axis of the reactor, once efficient light irradiation can be achieved by installing the UV lamp at the center of the tubular reaction system [57]. Volume of reactor and UV lamp were calculated at about 1018 cm³ and 177 cm³, respectively. The useful volume of the reactor, obtained by subtracting the reactor volume by the volume of the UV lamp, was approximately 841 cm³. In the useful volume of the reactor (area of annular space) was introduced a glass fiber filter forming a packed bed. To be negligible, the volume occupied by the glass fiber filter was disregarded in calculating the useful volume of the reactor. During packaging, one filter mat of glass fiber was placed along the length of the reactor. Mirrored plastic film and dark plastic film were added on the external surface of the photoreactor to enhance the lighting capacity of the UV lamp due to reflection (scattering) and to let opaque to ultraviolet light the surface of the reactor for an observer positioned externally to the reactor, respectively. Coating of mats fabricated of thin and long fibers offers advantages as: exposes a large photocatalyst surface area, performs silent operation conditions, the open structure enables sufficient light penetration, experiences only limited pressure drop and exerts sufficient filtering capacity [58]. Consequently, the purpose was to develop a convenient reactor design along with a practical photocatalyst coating on glass fiber filters suitable for real-scale application. Figure 2 presents the cross section view of the photoreactor.

2.4. Experimental device and procedure

Experimental set-up designed for the photocatalytic removal of H₂S in air is schematically presented in Figure 2. The set-up consists of four main sections: (i) air generation system; (ii) H₂S source; (iii) photocatalytic reactor previously described; (iv) H₂S measure ports. The carrier gas was generated by an air compressor, which draws in ambient air and leads to a series of filters (oil filter, activated carbon filter and particulate filter) for purification. Then, the fluid was conducted to gas flow meters, properly calibrated for the operating conditions, for direct measure of instantaneous volumetric flow. Generation of hydrogen sulfide in gas-phase can be found elsewhere in more details [33]. Briefly, the desired pollutant concentrations can be obtained by changing the pH of the sulfide solution or carrier gas flow rate. The irradiance of ultraviolet radiation emitted by the UV lamp was measured using a radiometer (General, UV513AB) in a range between 280–480 nm. The

temperature (T) and the relative humidity (RH) of the gas stream were measured immediately after the photocatalytic reactor outlet (Instrutherm, C-2). Concentration of H₂S was measured using a portable multi-gas analyzer (Drager, X-am 7000). The efficiency (η) of the PCO process was expressed in terms of degradation of H₂S, calculated as follows:

Photocatalytic efficiency (%) = $\frac{[H_2S]_{inlet} - [H_2S]_{outlet}}{[H_2S]_{inlet}} \ge 100$

Where, $[H_2S]_{inlet}$ is hydrogen sulfide concentration at the reactor inlet and $[H_2S]_{outlet}$ is the hydrogen sulfide concentration at the reactor outlet, in ppm_v. The residence time (τ) can be calculated using V (reactor volume) and Q (flow rate), according to the following equation:

 $\tau = \frac{V}{Q}$

2.5. Photocatalytic degradation of H₂S

Photocatalytic degradation of H_2S was performed in two steps: (i) experiments were conducted only with the presence of UV lamp to evaluate the photolysis of the pollutant; (ii) TiO_2 glass fiber filters were inserted into the reactor to conduct the photocatalytic tests. The runs started when the adsorption equilibrium between the pollutant and the experimental apparatus was established in the dark. This process provides an indication of the adsorption affinity between the reactor, the photocatalyst and the pollutant, and is important to verify that there were no leaks in the experimental system. The occurrence of equilibrium is assured when the inlet and outlet concentrations of H_2S in the reactor become identical. Adsorption phenomenon in photocatalytic systems is dependent on many parameters (e.g., flow rate;

(3)

pollutant concentration; reactor shape; type, property, mass quantity and support material of the photocatalyst). Hence, to reach gas-solid adsorption equilibrium depends from case to case. In this work, gas-solid adsorption equilibrium in the dark was achieved in no more than 20 min during all tests. Then, the UV light was switched on to start the experiments, and the H₂S degradation was monitored as a function of time by measuring the H₂S concentration. Sampling procedures were performed at intervals of 5 min at the reactor inlet and outlet, during 60 min, in triplicates for each run. Relative humidity (65%), dosage of photocatalyst (4 g.l⁻¹), UV irradiance (0.39 mW.cm⁻²), oxygen content (20.9%) and temperature (~ 27.4 °C) were kept constants in all tests. For the photocatalytic experiments, the operating conditions volumetric flow rate and inlet pollutant concentration were varied from 25 l.h⁻¹ to 150 l.h⁻¹ (residence time from 121 s to 20 s) and from 12 ppm_v to 163 ppmv of H₂S, respectively.

Photodegradation reactions occur on the surface of a photocatalyst. Therefore, limitations can occur due to mass transfer of reactants to the surface. This limitation is relevant for situations where the reactions occur quickly and the mass transfer is slow. In tubular reactors, limitations due to mass transfer were observed in systems whose inner walls of the tube had fairly large diameter in relation to its length [59]. Reynolds number was calculated for flow rates from 25 1.h⁻¹ to 150 1.h⁻¹ to estimate the type of regime. Therefore, interstitial velocity varied from 0.018 m.s⁻¹ to 0.0029 m.s⁻¹ with a Reynolds number ranging from to 7 to 41. A plug-flow reactor was adopted for kinetic modeling because this type of reactor is characterized by operating under laminar flow conditions. Hence, for comparison purposes of the experimental program analyzed herein, it was assumed that the photoreactor is a conventional pseudohomogeneous, isothermal and one-dimensional plug-flow, although the radiation field is not uniform.

2.6. Kinetic modeling

Regarding to catalyst systems, a convenient supposition is that the pollutant photooxidation can be described by Langmuir–Hinshelwood (L-H) approach [60], considering monolayer coverage, uniform surface, all adsorption sites are equivalent and there is no interaction between adsorbates [61]. According to this theory, the equation for photocatalytic reactions rate (r) is given by the well-known equation:

$$r = -\frac{\text{kKC}}{1 + \text{KC}}$$

Where, k is the reaction rate constant, related to the limiting rate of reaction at maximum coverage for the experimental conditions; K is the adsorption equilibrium constant and reflects the proportion of solute molecules which adhere to the catalyst surface; and C is the target pollutant concentration [62]. Combining Equation 4 with the mass balance of a plug-flow reactor operating at steady state, the Equation 5 is obtained [62, 63]:

$$\frac{V}{Q} = \frac{1}{kK} \ln(C_{inlet}/C_{outlet}) + \frac{1}{k}(C_{inlet} - C_{outlet})$$

(5)

(4)

Where, Q and V represent the volumetric gas flow rate and the reactor volume, respectively. The ratio V/Q is the residence time (τ), which represents the average time a molecule takes to pass through the reactor; C_{outlet} is the pollutant concentration at the reactor outlet and C_{inlet} is the inlet pollutant concentration. Equation 5 is valid assuming negligible mass transfer effects and effect of intermediates compounds formation [64]. After linear rearrangement Equation 5 can be written as follows [65, 66, 67, 68]: Plotting ln(C_{inlet}/C_{outlet})/(C_{inlet} - C_{outlet}) *versus* (C_{inlet} - C_{outlet})⁻¹ with experimental data should be linear if the L-H model describes appropriately the process. The slope of the regression line represent the product of τ , k, K and the intercept –K [68]. Equation 6 can be tested using different values of V/Q, either by varying the reactor volume or the flow rate or the inlet pollutant concentration [62, 63].

3. Results and Discussion

3.1. SEM/EDS and FEG-SEM

SEM coupled with EDS and FEG-SEM technics were applied to visualize the external surface morphology, thickness and elemental composition of TiO₂ thin films formed on the glass fiber. SEM micrographs and EDS spectra are shown in Figure 3.

After one coating (Figure 3-A) was observed the presence of particles heterogeneous dispersed on the glass fiber surface In Figure 3-B, after two coatings, existing particles increased significantly, indicating greater deposition. However, regions with discontinuities were still observed. After three coatings (Figure 3-C) the coating was substantially uniform and well distributed in the longitudinal direction of the glass fiber surface. The presence of C (catbon), O (oxygen), Na (sodium), Mg (magnesium), Si (silicon), Ca (calcium), Au (gold) and Ti (titanium) peaks were identified. The peaks of C, O, Na, Mg, Si and Ca can be mainly attributed to the natural glass fibers composition and possible organic residues remaining on the material surface after cleaning. Peaks of Au is due to sputtering of the samples with gold ions. Here, EDS analyses were used only qualitatively without the relative amount of elements. Nevertheless, peaks of Ti increasing intensity suggests that the mass amount of

TiO₂ was higher after each coating procedure. Accordingly, the need to repeat the immersion process and heat treatment for 3 times were confirmed.

The morphology of TiO₂ thin films is presented by FEG-SEM micrographs (Figure 4). Figure 4-A and Figure 4-B show the TiO₂ thin film after 3 coatings at higher magnifications. Clusters of TiO₂ nanoparticles with high roughness and porosity were formed on the glass fiber surface, as seen in Figure 4.

SEM micrographs shown in Figure 5 presents the cross-section of the TiO₂ thin film formed on the surface of the glass fiber after 3 coatings. The thin film thickness was estimated at approximately 1.8 μ m (Figure 5-A). TiO₂ thin film and the glass fiber are indicated by arrows in a closer view in Figure 5-B.

3.2. XRD

To determine the phase composition and the crystallite size of TiO₂ P 25 nanoparticles, XRD analyses were conducted. Figure 6 shows the XRD patterns of Sample 1 (TiO₂ P 25 powder as received) and Sample 2 (TiO₂ P 25 powder after the heat treatment). The crystalline phases identified in the diffractograms of Sample 1 were anatase (JCPDS 01-071-1167) and rutile (JCPDS 01-073-2224); and anatase (JCPDS 01-071-1166) and rutile (JCPDS 01 072-1148) for Sample 2. The ratio of 90.3% for anatase (202243 ICSD) and 9.7% for rutile (JCSD 16636) were determined for both samples by the Rietveld method. Similar results (90% anatase and 10% rutile) were found in the work of Le et al [69]. In other studies, the P 25 consisted of anatase and rutile phase in a ratio of about 3:1 [41, 70]; and a fraction of about 80% anatase and 20% rutile [63, 71, 72, 73]. The ratio of anatase and rutile is approximately 80/20, acoording to the manufacturer. Regarding to reproducibility of the P 25 crystalline composition, Ohtani et al [74] observed changes in the ratio from time to time even for samples collected from the same package, suggesting that P 25 is a simple mixture composed of anatase (predominantly), rutile and amorphous phase (minority) titania with different ratios depending on the sample production batch and position in a package. The composition phases of P 25 from the same batch investigated in this paper were analyzed previously (data not shown) also by XRD, and the proportion of 90.2% anatase and 9.8% rutile was determined. Therefore, variation in the ratio between the crystalline phases of P 25 was not clearly observed.

XRD patterns also provide information about the width and intensity of the peaks. The intensity of the diffraction peaks, in general, is related to crystallization. The width of the peaks is related to crystallite size [74]. As can be seen in Figure 6, diffractograms remained practically unchanged, indicating similar crystallite size and crystallization of the samples. According to Equation 1, the values calculated for the diameter of TiO2 nanoparticles of Sample 1 and Sample 2 were 22.1 nm (most intense diffraction peak position of 25.307°) and 22.2 nm (most intense diffraction peak position of 25,270°), respectively. The crystallite size of Sample 1 is consistent with the results reported in the literature for P 25 powder. As stated by manufacturer (Evonik Industries), the primary particles have a mean diameter of approximately 21 nm. For example, the particle size of P 25 found in previous studies were 20 nm [75], 26 nm [76], 26.9 nm [77], 30 nm [49, 63, 72], 30.1 [78]. In fact, the primary particle size of P 25 is in the range of 20 – 50 nm [69]. The temperature used (120 °C) for the heat treatment was selected to avoid changes in the properties of the photocatalyst and support material. The anatase phase has low thermal stability and transforms to rutile phase, which is more stable, between 400 and 500 °C [79]. For exemple, Bowering et al. [80] studied the calcination temperature on the composition of P 25 and observed that the temperatures higher than 450 °C transformed a fraction of anatase in rutile. In this paper, no alteration in the crystalline phases of titanium dioxide was observed as expected. Consequently, the heat

treatment was used to improve the adhesion between the photocatalyst and the glass fiber, besides removing the reagents used in the thin films formation.

3.3. Evaluation of photolysis

Photolysis was evaluated to ensure that the photocatalytic reaction was exclusively responsible for hydrogen sulfide degradation. When the adsorption equilibrium was reached in the dark, the lamp was switched on. Figure 7 presents a photolysis experiment, in triplicate, conducted for a flow rate of 50 $1.h^{-1}$ ($\tau = 60.5$ s) and H₂S inlet concentration from 26 to 32 ppm_v.

The outlet concentration was higher than inlet concentration at some points. This is due to the H₂S generating solution not to be perfectly stable at a fix value, resulting in differences in the inlet and outlet concentrations. However, this variability was negligible as demonstrated by the error bars in Figure 7 and it can be concluded that only the UV light here used proved not contribute to the degradation of the target pollutant. Canela et al. [33] studied the photocatalytic degradation of H₂S using a black light lamp of 30 W with a peak light intensity of 365 nm and also found that the direct photolysis of the compound was negligible. In fact, inorganic gases have a low coefficient of light absorption in the ultraviolet region [81]. Moreover, absorption by H₂S occurs in the region between 190 nm and 270 nm for photolysis in gaseous matrices at low temperatures [82]. Therefore, as expected, degradation of the target pollutant via photolysis was unsatisfactory, since an ultraviolet lamp of 365 nm UV-A radiation was used. The irradiance of ultraviolet radiation emitted by the lamp was measured at 0.39 mW.cm⁻².

Volumetric flow rate was investigated in the range of $25 - 150 \text{ l.h}^{-1}$, while other operating conditions, such as H₂S inlet concentration, relative humidity, temperature, dosage of photocatalyst, UV radiation, were kept constant. The H₂S removal efficiencies were calculated using Equation 2 and are shown in Figure 8, where the markers represent the mean value of the triplicate and the bars the standard error associated for each flow rate. Regardless of the volumetric flow rate, the system took about 15 min for stabilization. The period of initial activation observed in Figure 8 is a transient state due to the changes on the TiO₂ surface caused by the UV radiation [12]. The maximum removal efficiency (i.e., \sim 73%) was obtained with the lowest flow rate (i.e., 25 1.h⁻¹), which corresponds to a residence time of approximately 121 s. No effects of flow rate on the adhesion of photocatalyst on the glass fiber were observed. Experiments of evaluation of the volumetric flow rate on the H₂S photocatalytic removal found similar results [9]. The same remarks about volumetric flow rate and residence time were observed to other inorganic pollutants, e.g., NH3 [63] and for VOCs, e.g., toluene [64], trimethylamine and isovaleraldehyde [83]. Generally, lower flow rates result in higher removal efficiencies because the residence time is greater. When the flow is increased, the residence time is reduced (inversely proportional). This behavior is explained in terms of the competition between the residence time in the reactor and the contact probability of the pollutant with the photocatalyst [57, 63].

3.5. Evaluation of H₂S inlet concentration

H₂S inlet concentration was investigated in the range of $12 - 163 \text{ ppm}_v$, while the volumetric flow rate was kept constant at 25 l.h⁻¹ ($\tau = 121 \text{ s}$). This strategy was adopted to increase the photocatalytic efficiency of H₂S previously performed. Figure 9 shows the results of the evaluation of four ranges of H₂S inlet concentration in the reactor, where the markers

represent the mean value of the triplicate and the bars the standard error associated for each inlet concentration range.

As seen in Figure 9, the removal rate in terms of photocatalytic efficiency tends to decrease as the inlet concentration increases. The experiments carried out with H₂S inlet concentration in the range of 12 - 14 ppm_v reached the highest degradation efficiencies (i.e., ~ 99%). It can be assumed that at high concentrations of pollutants the OH• generation on the surface of the photocatalyst is compromised, since the active sites are saturated with adsorbed compounds. Thefore, the removal efficiency is decreased due to fixed amount of available active sites on the surface of TiO₂ [63, 65, 67, 83]. Despite the experimental conditions are different, the same findings regarding to the inlet pollutant concentration were observed by Li et al. [10] in a study involving photocatalytic degradation of H₂S using continuous flow mode. Similar results were found in the degradation of VOCs, such as trichlorethylene [66], ethylene [84], trimethylamine and isovaleraldehyde [83]. Usually, there is an optimal pollutant concentration that will maximize the photocatalytic oxidation reaction rate when the other conditions remain stable [85]. According to the L-H theory, any further increase of the inlet concentration will not result to a proportional increase of the degradation rate [65].

3.6. Long-term use

To evaluate the deactivation time of TiO₂ thin films formed on glass fiber filters the long-term use experiment was carried out. For this purpose, gas samples were measured at the reactor inlet and outlet every 30 min. Figure 10 presents the test performed using optimal operating conditions found in previous experiments (i.e., $Q = 25 \text{ l.h}^{-1}$; $\tau = 121 \text{ s}$; $C_{inlet} = \sim 18 \text{ ppm}_v$ of H₂S; RH = 65%; O₂ = 20.9%; T = 27.4 °C). During 16 h of experimentation a photocatalytic efficiency of more than 89% was maintained (indicated in

Figure 10 as 89% line efficiency) for H₂S removal. The deactivation of the TiO₂ glass fiber filter was not observed and the efficiency of the PCO process was at 64% after 28 h of continuous use (indicated in Figure 10 as 64% removal efficiency).

Since the process occurs in the gas phase, the SO_4^{2-} formed remains adsorbed on the photocatalyst [12]. Consequently, sulphate formation is an inherent problem, since this compound accumulates on the TiO₂ surface covering the active sites and leading to progressive deactivation of photocatalyst until complete deactivation [12, 34]. For example, Portela et al [12] observed a maximum removal efficiency of approximately 80% after 2 h of experimentation on laboratory scale. This percentage was kept constant for 2h, totaling 4 h, until it was observed a decrease in photocatalytic activity due to accumulation of SO4²⁻ on the surface of TiO2. These experiments were generally conducted with H2S inlet concentration of 15 ppm_v, 1.3% of relative humidity (synthetic air) and residence time of 3.6 s (flow rate of 75 ml.min⁻¹). The comparison of results in photocatalytic studies is not feasible due to the number of factors involved in the process. However, directly comparing the results obtained by Portela et al [12], the residence time applied here (121 s) was higher than their residence time (3.6 s). This parameter is possibly the responsible for the relatively fast deactivation of the photocatalyst in the work of Portela et al [12]. In a study of photocatalytic degradation and photolysis using ozone [10] H₂S removal decreased from 99.60% to 81.58% after 30 h of experimentation. This value dropped to 25.88% after 50 h, suggesting that the TiO₂ was finally being saturated. The main disadvantage of using TiO₂ thin films to H₂S removal is, hence, the formation of SO₂ and SO₄²⁻. Sulphur dioxide is toxic, corrosive and has an unpleasant odour. The accumulation of SO4²⁻ on photocatalyst surface leads to deactivation of TiO₂[12]. Although no supporting data is shown and reaction mechanisms of photocatalytic degradation of H₂S over TiO₂ have continued not to be fully understood until now, the hypothesis that SO₄²⁻ contributes or is responsible for deactivation of the photocalyst seems

plausible according to previous works [40]. Regarding to the packing material, glass fiber mats are relatively inexpensive, lightweight, efficiently scatters light, highly stable against UV radiation and easily adaptable to different shapes [86].

3.7. Kinetics of the photocatalytic degradation of H₂S

Kinetic modeling of the photocatalytic degradation reaction of H₂S was performed according to Langmuir-Hinshelwood (L-H) approach and reactor hydraulics (i.e., assuming plug-flow regime). L-H theory was applied to fit H₂S inlet concentration experimental data. Figure 11 presents the plot of ln(Cinlet/Coutlet)/(Cinlet - Coutlet) versus (Cinlet - Coutlet)⁻¹, as described previous by Equation 6. The solid line represents the multiple linear regression fit of the model to the experimental data, while the dashed lines represent the 95% confidence interval. The circle markers are inside the confidence interval, indicating statistical significance. In fact, when good linearity is observed in the degradation of a pollutant, the treatment via L-H model applicability is appropriate [37]. Here, the value of R² of 0.98 was found. The square markers represent the runs performed for the inlet concentration ranges of $87 - 110 \text{ ppm}_{v} (3.5 - 4.5 \text{ mmok} \text{m}^{-3}) \text{ and } 122 - 163 \text{ ppm}_{v} (4.9 - 6.6 \text{ mmol} \text{m}^{-3}).$ In these ranges, L-H approach were not modeled due to distinct removal efficiency patterns, mainly caused by non-achievement of the steady-state, as observed in Figure 9. Moreover, the influence of intermediate products and the effect of the mass transfer probably can not be neglected in the mentioned ranges. However, the photocatalytic degradation of H₂S was represented by L-H model with respect to inlet concentration experimental data in the range from 12 to 40 ppm_v $(0.5 - 1.6 \text{ mmol.m}^{-3})$.

Table 1 presents the parameters extracted from multiple linear regression of the photocatalytic degradation of H₂S according to L-H approach combined with a plug-flow reactor operation. The reaction constant (k) was determined at approximately

10.5 µmol.m⁻³.s⁻¹ and the adsorption constant (K) of approximately 5,263 m⁻³.mol. In fact, k and K can be considered as apparent constants, because the mass transfer contribution is intrinsically included in the calculation. Determination of reaction kinetics in photocatalytic systems is an important step for applications such as reactors design, sizing, optimization and prediction [46, 58, 87].

4. Conclusions

To investigate photocatalytic degradation of H₂S, a convenient, economical and facile coating approach of TiO₂ thin films on glass fiber filters packed in an annular photoreactor was developed. The support material was packed in an annular photoreactor in order to evaluate the photocatalytic removal of the target pollutant, SEM, EDS, FEG-SEM and XRD analyses confirmed the chemical deposition of the photocatalyst (TiO2) on the glass fiber and showed the morphological properties of the thin films, besides the crystalline phases and crystallite size of TiO2 Clusters of TiO2 nanoparticles with high roughness and porosity were formed. XRD patterns exhibited that the heat treatment to which the photocatalysts were applied did not change TiO2 crystalline phases (90.3% for anatase and 9.7% for rutile samples before and after heat treatment) as expected and the crystallite size (measured in 22.1 nm for the sample as received and 22.2 nm for the sample after heat treatment). Photolysis experiments showed that only the UVA (365 nm) was not able to promote the degradation of H₂S. PCO efficiencies of 73% was achieved for a flow rate of 25 1.h⁻¹ (τ = 121 s) and H₂S inlet concentration of 20 - 60 ppm_v and 99% for H₂S inlet concentration from 12 - 14 ppm_v and iqual flow rate. During the long-term use, the photocalytic efficiency remained higher than 89% for 16 h. After this period, the decrease in photocatalytic activity was observed. Nevertheless, even after 28 h of continuous experimentation, the PCO efficiency was at 64% and the gradual deactivation of the photocatalyst was not observed. The LangmuirHinshelwood approach combined with the mass balance of a plug-flow reactor was applied and the reaction constant (k), 10.5 μ mol.m⁻³.s⁻¹, and adsorption constant (K), 5,263 m⁻³.mol, were obtained from fitting (R² = 0.98) the experimental data of H₂S inlet concentration in the range from 12 to 40 ppm_v (0.5 – 1.6 mmol.m⁻³). To promote applications as reactors design, sizing, optimization and prediction processes the determination of reaction kinetics is a fundamental step.

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Figure Captions

Fig. 1. Schematic diagram of TiO₂ thin films formation on filter mats fabricated of glass fiber.

Fig. 2. Schematic diagram of the experimental apparatus.

Fig. 3. SEM micrographs and EDS spectra of the TiO₂ thin films formed on the glass fiber: (A) one coating

(50 µm bar); (B) two coatings (50 µm bar); (C) three coatings (50 µm bar).

Fig. 4. FEG-SEM micrographs of the TiO₂ thin film formed on the glass fiber after 3 coatings: (A) 10 μm bar;(B) 100 nm bar.

Fig. 5. SEM cross-section micrographs: (A) TiO2 thin film formed on the glass fiber after 3 coatings (10 µm

bar); (B) detail of the external morphology of the TiO₂ thin film (5 μm bar).

Fig. 6. XRD patterns of Sample 1 (TiO₂ P 25 powder as received) and Sample 2 (TiO₂ P 25 powder after the heat treatment).

Fig. 7. Evaluation of photolysis on the H₂S removal. The markers represent the mean value of the triplicate and the bars the standard error associated for each concentration. Operating conditions: $Q = 50 \text{ l.h}^{-1}$; $\tau = 60.5 \text{ s}$;

 $C_{inlet} = 26-32 \text{ ppm}_v \text{ of } H_2 S.$

Fig. 8. Evaluation of the volumetric flow rate on the photocatalytic oxidation of H₂S. Operating condition:

 $C_{inlet} = 35-40 \text{ ppm}_v \text{ of } H_2 S$. The markers represent the mean value of the triplicate and the bars the standard error associated for each flow rate.

Fig. 9. Evaluation of the inlet concentration on the photocatalytic oxidation of H₂S. Operating condition:

 $Q = 25 \text{ l.h}^{-1}$. The markers represent the mean value of the triplicate and the bars the standard error associated for each inlet concentration range.

Fig. 10. Evaluation of TiO₂ photocatalytic glass fiber filter deactivation. Operating conditions: $Q = 25 \text{ l.h}^{-1}$; $\tau = 121 \text{ s}$; $C_{inlet} = 18 \text{ ppm}_v \text{ of } H_2 \text{S}$.

Fig. 11. Kinetic modeling of the photocatalytic oxidation reaction of H₂S according to Langmuir-Hinshelwood (L-H) approach combined with plug-flow reactor hydraulics.

Table Caption

Table 1

Multiple linear regression parameters for the photocatalytic oxidation of H₂S according to Langmuir-Hinshelwood (L-H) approach along with a plug-flow regime.

 Table 1

 Multiple linear regression parameters for the photocatalytic oxidation of H₂S according to Langmuir-Hinshelwood (L-H) approach along with a plug-flow regime.

k (µmol.m ⁻³ .s ⁻¹)	K (m⁻³.mol)	R	R ²	Adjusted R ²	р	Ν
10.5	5,263	0.99	0.98	0.97	0.0002	6

Accepted Manuschi





















