

Gas-phase destruction of H₂S using TiO₂/UV–VIS

Maria C. Canela, Rosana M. Alberici, Wilson F. Jardim *

Instituto de Química, Universidade Estadual de Campinas, CP 6154, CEP 13083-970 Campinas, SP, Brazil

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Abstract

Photocatalytic destruction of H₂S using TiO₂/UV–VIS was conducted in the gas-phase. This process showed high efficiency, reaching degradation yields of 99% at concentration ranges of 33 to 855 ppmv. Oxygen was shown to be necessary for the photodestruction of H₂S. Conversion rates were small in experiments conducted under nitrogen atmosphere (17%) compared with experiments in the presence of oxygen (99%). The photocatalytic activity of TiO₂ showed that at 217 ppmv, there was no loss of the activity over extended operation periods. Deactivation of the catalyst was observed only when working at higher H₂S concentrations (such as 600 ppmv), and is assumed to be caused by the adsorption of the byproducts produced onto the catalyst surface. The main product in the photocatalytic destruction of H₂S in gas-phase detected by FTIR and for turbidimetric analysis was sulfate ions. A mass balance showed that H₂S is oxidized to SO₄²⁻ (95% of SO₄²⁻ were easily recovered from the catalyst surface), and that only 0.02% of this ion was detected at the reactor effluent. Experiments carried out using the photocatalytic process to minimize noxious emission of H₂S stripped from a raw sewage sample showed that this process is viable for the elimination of odor in wastewater treatment plants. © 1998 Elsevier Science S.A.

Keywords: H₂S; TiO₂; Photodestruction; Odor; Gas-phase

1. Introduction

The problem with malodorous emissions next to sewage and industrial wastewater treatment plants has been largely discussed because it is a nuisance in the neighborhood. The odors are mainly caused by sulfurous compounds such as mercaptans, organic sulfides, disulfides and above all, hydrogen sulfide (H₂S), which has an extremely low odor threshold (0.0004 ppm), is highly toxic and has a characteristic rotten-egg smell [1]. Long exposure to a concentration of 0.03% (300 ppm) of H₂S in the air has caused death, and concentrations exceeding 2000 ppm can be fatal if humans are exposed for but a few minutes [2]. The generation and emission of H₂S from wastewater treatment facilities is a maintenance problem because of its noxious odor, health hazard and severe corrosive attack on process equipment. It has been observed that the main sources of odor at such facilities are the thickeners (H₂S, CH₃SH, NH₃), thermal processing (H₂S, acetaldehyde), dewatering (H₂S, NH₃) and storage (NH₃) [3].

The conventional technologies used to remove volatile inorganic and organic compounds present in wastewater can be classified as destructive and non-destructive processes.

Adsorption using activated carbon is an example of a non-destructive process which involves simply phase transfer of the pollutant. In the destructive processes, such as incineration, although the toxic compounds are oxidized, sometimes the byproducts formed may be more hazardous than the original compounds. Some alternative processes include the use of oxidizing agents (H₂O₂, Cl₂, Na/CaOCl, KMnO₄, NaOCl/NaOH, etc.) or removal by precipitation with ferrous/ferric sulfate [2,4,5]. In the gas-phase, biofilters, packed-tower scrubbers and activated carbon adsorption are the most used processes [4,6–9].

The destruction of toxic volatile compounds in the gas-phase using TiO₂/UV–VIS has been investigated because it offers several advantages when compared to the other processes. Since the destruction is made at room temperature and ambient pressure, it is not necessary to use additional reagents and the final products show little or no toxicity, compared to the parent compounds. It has already been demonstrated that this process can be used to destroy a wide range of organic compounds [10–12]. However, the photodestruction of inorganic compounds as well as sulfur-containing compounds has been little explored [13–15]. In an interesting work developed by Suzuki et al. [16] the TiO₂ photocatalytic process was used for the elimination of some atmospheric odorous compounds, among them, H₂S. The H₂S destruction in gas-

* Corresponding author. Tel.: +55-19-788-7012; fax: +55-19-239-3805; e-mail: wjjardim@iqm.unicamp.br

phase using near TiO₂/UV–VIS has also been studied by Jardim and Huang [17]. These authors observed high degradation yields (97.2%) when using H₂S at relatively low concentrations (30 ppmv) with a 500 ml min⁻¹ flow rate.

In this work, the optimization of photocatalytic destruction of H₂S in the gas-phase was studied and some important parameters, such as the role of O₂, H₂S concentration, flow rate and photocatalytic deactivation, were addressed. Final products of H₂S oxidation were investigated using the FTIR technique. The destruction of H₂S emitted from a sewage sample was carried out under laboratory conditions, and the results obtained showed that this process can be used with success to destroy malodorous emissions from this source.

2. Experimental

2.1. Materials

The Environmental Chemistry Laboratory, where this research was carried out (Institute of Chemistry, State University of Campinas) works under Good Laboratory Practices (GLP). Titanium dioxide powder was obtained from Degussa (P-25) with a primary particle diameter of 30 nm, a crystal structure of primarily anatase (70% anatase and 30% rutile) and a surface area of $50 \pm 15 \text{ m}^2 \text{ g}^{-1}$ (BET). The catalyst was used without further pretreatment. All the chemicals used were of analytical-reagent grade and distilled water was used for preparing solutions.

2.2. Photodegradation apparatus

An annular plug flow photoreactor was constructed using a glass cylinder measuring 855 mm with a 35 mm internal diameter and a total volume of 405 ml. The reactor has a cross-sectional area of 4.73 cm². The catalyst was coated onto the internal glass surface using an aqueous slurry, followed by drying with hot air. The coating was repeated several times until the tube was opaque to ultraviolet light measured at 366 nm (Cole-Parmer radiometer series 9811). A TiO₂ loading density of 3.2 mg cm⁻² was obtained by weighing the tube before and after the coating. A TiO₂ film thickness of ca. 5.3 μm was estimated by Scanning Electron Micrograph technique (SEM). Illumination was provided by a 30 W black-light lamp (Sankyo Denki Japan, BLB) with maximum light intensity output at 365 nm. The lamp was fixed at the center of the reactor. The light flux delivery to the reactor was determined to be 7.56×10^{-9} einsteins cm⁻² s⁻¹ measured using potassium ferrioxalate actinometry [18]. The working temperature of the reactor was $50 \pm 2^\circ\text{C}$ due to the heat delivered by the light source.

The basic experimental setup used in this study is shown in Fig. 1. It consists of a synthetic air (21% oxygen and 23% relative humidity) or nitrogen carrier gas contaminated with a known concentration of H₂S. The mixture was passed through the photoreactor in the absence of UV–VIS illumi-

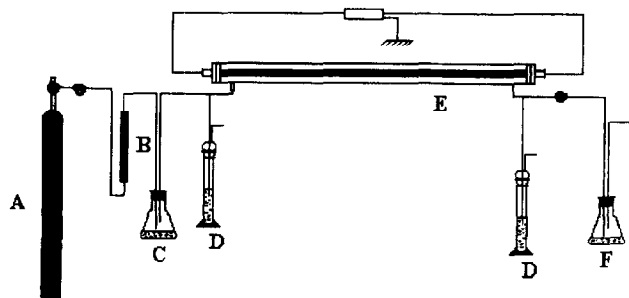


Fig. 1. Scheme of the experimental apparatus utilized for H₂S degradation. (A) Synthetic air, (B) flow meter, (C) conical flask with sodium sulfide solution or wastewater, (D) trapping solution for H₂S, (E) TiO₂/UV reactor e. (F) alkaline trap.

nation until gas–solid adsorption equilibrium under the flow was established, as indicated by identical inlet/outlet H₂S concentrations. Then, UV–VIS illumination was turned on and the conversion rate was monitored as a function of time by measuring the concentration of H₂S before and after passing through the photoreactor. A steady-state was normally achieved 30 min after the light was turned on. This system provided a final relative humidity of ca. 80%. This humidity level (40–60% corresponding to 11,000–16,000 ppmv) is close to the humidity range normally found in most working environments. Control samples were investigated by passing the contaminated air through a catalyst-free reactor. After finishing the experiments, the reactor was flushed for 30 min in the dark using synthetic air to restore the initial conditions before running the next experiment. In all experiments described in this work, the gas-flow rate (controlled by mass flow controllers and determined using flowmeters, McMillan) varied from 164 ± 2 to $1500 \pm 30 \text{ ml min}^{-1}$, and the H₂S was photodegraded at initial concentrations between 30 and 855 ppmv. Repeatability obtained for 8 complete runs (including all the analytical steps) was 1.1%.

2.3. Hydrogen sulfide source

A novel and simple device was used for the generation of hydrogen sulfide. The system was based upon the continuous generation of the gaseous species (H₂S) due to rigid pH control of a sodium sulfide solution. This H₂S generator solution was made with 0.6 g of Na₂S·9H₂O and 1.44 g of Na₂HPO₄ in 100 ml of distilled water, and the pH was initially fixed at 8.1 ± 0.1 using 1 mol l⁻¹ orthophosphoric acid. Under these experimental conditions, when synthetic air was forced to flow over the head space of this flask (without stirring) at 200 ml min⁻¹, an atmosphere containing 250 ppmv of H₂S was generated. The concentration could be kept constant around this value ($\pm 10\%$) for at least 5 h, and the solution was freshly prepared for each experiment. By changing the pH of the sulfide solution (from 4 to 12) and the carrier gas flow rate, atmospheres containing 855 down to 30 ppmv of H₂S were obtained. The generator device required an equilibrium period of 30 min to reach reproducible values for the generation of H₂S.

2.4. Determination of H₂S and byproducts

The H₂S concentration was measured by trapping the carrier gas in either 25.0 or 50.0 ml solutions of 0.1 mol l⁻¹ NaOH, using a washing bottle with a glass diffuser. Colorimetric determination of H₂S was carried out in the trapped solution using the Standard Methylene Blue Method (4500 S²⁻-D) [19].

Byproducts formed in the photodegradation were investigated using infrared (IR) analysis of the pure TiO₂, as well as the catalyst after the exposure to H₂S plus irradiation, and H₂S in the dark. The IR analysis was carried out using KBr disks in the region of 4000–400 cm⁻¹ using a FTIR-Perkin Elmer-1600.

Sulfate ions, generated during the photocatalytic destruction of H₂S, were eluted from the TiO₂ surface using 200 ml of water and determined by Standard Turbidimetric Method (4500-SO₄⁻²E) [19]. This result enabled to establish the mass balance between H₂S consumed and sulfate recovered.

2.5. Raw sewage sample

A raw sewage sample collected at the Santa Genebra Sewage Treatment Station was stored in the laboratory under anaerobic conditions for 20 days at 4°C, and used as a H₂S generator to feed the photocatalytic system. In this case, 500 ml of the sewage sample with pH adjusted to 4.5 with H₃PO₄ was continuously stripped using synthetic air at 250 ml min⁻¹. Under these conditions, a stream of contaminated air containing 154 ppmv of H₂S was obtained.

Some characteristics of the sewage sample, such as TOC, pH, total suspended solids and total volatile solids are shown in Table 1. Total organic carbon (TOC) analysis was made using a SHIMADZU-TOC 5000. Total suspended solids were determined using pre-ashed GF/C Whatman filter paper, followed by drying at 105°C. Total volatile solids were determined by igniting the filter at 500°C.

In this work, when the sewage sample was used at the original pH of 6.6 and stripped using 250 ml min⁻¹ of the carrier gas, an atmosphere containing 13 ppmv of H₂S was obtained. However, after adjusting the pH to 4.5, a 154-ppmv H₂S stream was obtained with this same flow rate.

Table 1
Characteristics of the raw sewage sample

Total suspended solids	256 (mg l ⁻¹)
Total volatile solids	240 (mg l ⁻¹)
TOC	141 (mg C l ⁻¹)
pH	6.6
S ⁻²	2.71 (mg l ⁻¹)

3. Results and discussion

3.1. The role of oxygen

Experiments were carried out in the presence and in the absence of oxygen. The results are presented in Fig. 2. The steady-state was achieved 30 min after the light was turned on. The direct photolysis of the compound, i.e., the decomposition in the absence of the catalyst, was negligible. The results confirm that in the absence of oxygen, using N₂ as carrier, the oxidation rate of H₂S was small, reaching just 17% after 120 min of irradiation (in this case, the steady-state). On the other hand, when in the presence of oxygen, the H₂S photodegradation reached 99% after 30 min of irradiation. Therefore, the presence of oxygen was shown to be necessary for the photodestruction of H₂S.

There have been many reports in the literature emphasizing the importance of O₂ in the photocatalytic reactions of organic substrates, although the exact role of oxygen in this process has not yet been completely established. For example, it has been observed that the photooxidation of CH₃Cl over rutile TiO₂ can be carried out on the catalyst surface in the absence of [•]OH and H₂O, but not in the absence of O₂ [20–22]. It is widely accepted that molecular oxygen is an efficient electron scavenger in the conduction band of the semiconductor, inhibiting the undesirable e⁻/h⁺ recombination process. Besides, oxygen is the precursor of various reduced (O₂^{-•}, HO₂^{-•}, HO₂[•] and H₂O₂) and very reactive species.

Hydroxyl radicals are often assumed to be the main charge-transfer species responsible for oxidation [23]. Recently, it has been suggested that degradation of organic compounds is not exclusively mediated via [•]OH radicals generated at the valence band, but that oxygen can play a more important role than a mere electron acceptor [24]. Results obtained by Hong et al. [25] showed that SO₂ photocatalytic oxidation occurs to a very small extent when conducted under N₂. The authors

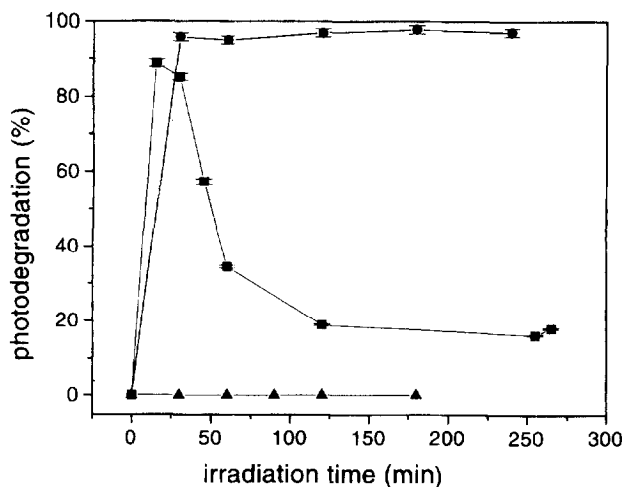


Fig. 2. The role of O₂ in the photodegradation of H₂S where (●) oxygen, (■) nitrogen and (▲) photolysis. Experimental conditions: Black-light lamp (30 W), Q = 250 ml min⁻¹, 80% relative humidity and [H₂S]_{input} = 250 ppmv.

observed that the reaction rate is independent of the dissolved oxygen concentration. They also proposed that oxygen is needed to accept conduction-band electrons to make valence-band holes available for the formation of radicals necessary to the photooxidation process.

It is interesting to note that at the beginning of the photo-degradation reaction, when nitrogen was used as the gas stream, the degradation yield was as high as when observed in the presence of oxygen. However, after a few minutes of irradiation, it dropped to only 17%. In these experiments in the absence of oxygen, the photoreactor was flushed with pure nitrogen for some time (typically 30 min), then the H_2S/N_2 mixture was introduced into the photoreactor. One can assume that this procedure was not drastic enough to remove the adsorbed oxygen on TiO_2 . In this case, a high degradation yield was expected at the beginning of the experiment, reaching no destruction when the adsorbed oxygen was consumed. Under this situation, the e^-/h^+ recombination process predominates and the rate of $\cdot OH$ radical formation decreases. Another possible mechanism that cannot be ruled out is the oxidation of the H_2S directly on the hole photoformed at the catalyst surface. Many works have assumed this to be the major mechanism in the first stage of direct oxidation for several organic compounds [26].

3.2. Effect of space time

Space time can be defined as the amount of catalyst (W) divided by the molar flow rate of H_2S (F) in the inlet stream [27]. The effect of space time on H_2S photooxidation was investigated using different flow rates (164 to 1500 $ml\ min^{-1}$) of the gas stream. These flow rates correspond to residence times between 0.27 to 2.46 min. It is worth mentioning that in the system used, the distribution of the catalyst along the annulus is not uniform. Although the layer of TiO_2 was ca. $5.3\ \mu m$ thickness only the surface is in the illuminated region. As long as it is not possible to determine the amount of catalyst actually receiving photons in the system, the total mass of catalyst in the reactor (3 g) was used in the calculation. Fig. 3 shows H_2S conversion as a function of the space time. The results indicate that increasing the space time resulted in an increase in the reaction conversion. Higher conversion was achieved for space time values above $1.04 \times 10^8\ g\ s\ mol^{-1}$, corresponding to a residence time of 1.73 min, or $234\ ml\ min^{-1}$ flow rate. The majority of the photocatalytic experiments were carried out with flow rates near this value.

3.3. Influence of the concentrations of H_2S

The oxidation rate can be defined as

$$r = (C_{in} - C_{out})Q/A \quad (1)$$

where C_{in} and C_{out} are the inlet and outlet contaminant concentration, respectively, Q is the volumetric flow rate, A is

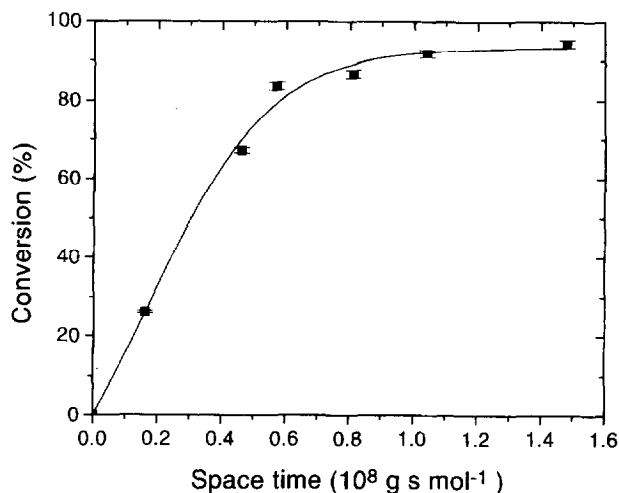


Fig. 3. Effect of space time on the reaction conversion of H_2S . Experimental conditions: Black-light lamp (30 W), 21% oxygen, 80% relative humidity and $[H_2S]_{input} = 166\ ppmv$.

the flow area. The rate term is normalized by the flow area as the illuminated or active area of the catalytic element is not precisely known. The ratio Q/A is the face velocity, i.e., the flow velocity entering the reactor.

The oxidation rate for H_2S as a function of the inlet concentration (30 to 855 $ppmv$) under a flow rate of $200\ ml\ min^{-1}$ is shown in Fig. 4. The reaction exhibits a pseudo-first-order dependence on H_2S concentration within the range of the concentration tested. Half-life values of 0.42 min and a rate constant of $1.637\ min^{-1}$ were obtained. The photodestruction of H_2S in the concentration range tested was kept constant at approximately 99%, independent of the feeding concentration. Studies of H_2S degradation in the gas-phase at higher concentrations (above 850 $ppmv$) were not carried out due mainly to the low probability of reaching these concentrations in atmospheres over wastewater facilities or any other areas where H_2S is generated [4,28].

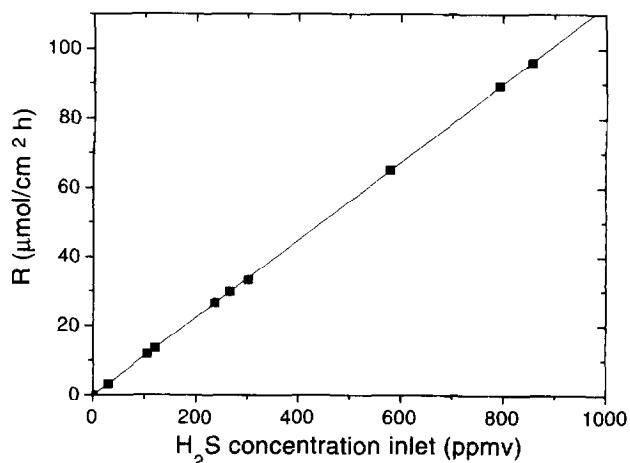


Fig. 4. Oxidation dependence on H_2S concentration. Experimental conditions: Black-light lamp (30 W), $Q = 200\ ml\ min^{-1}$, 21% oxygen and 80% relative humidity.

3.4. Long-term photocatalytic activity

A detailed investigation of the catalyst life and its possible deactivation was carried out in the presence of oxygen. In this particular study, H_2S degradation was monitored in a long term experiment (24 h) of continuous operation, using two different inlet concentrations. The results obtained in these experiments are summarized in Fig. 5. As can be noted, when working at 217 ppmv of H_2S , the photocatalytic activity was maintained for a long time of continuous use. However, at higher H_2S concentrations, such as 600 ppmv, degradation yields dropped from 99% down to 61% after 1 h of irradiation. This value dropped even further to 36% after 2 h, when the steady-state was reached. Interestingly, when the light is turned off for 30 min, the reactor seems to recover the initial activity for a short period of time, but rapidly returns to the same performance observed just before turning the light off.

This decrease in the photocatalytic activity could be caused by the adsorption of byproducts of the oxidation of H_2S . This hypothesis is related to the fact that sulfate ion was detected as a major product of H_2S oxidation. An analysis in the reactor outlet stream, using a trap containing BaCl_2 confirmed the formation of sulfate ions in small quantities (0.02%). Sulfate ions leaving the photoreactor are very likely present in the form of H_2SO_4 droplets due to the humidity in the air stream. The major portion of the photogenerated sulfate remains attached to the catalyst surface, and it is easy to assume that this ion is acting as a competitor for the adsorption sites at the catalyst. It appears that when the light is turned off, the original activity is restored for a short period of time due to either the desorption at the catalyst surface, or to the build up of oxygen concentration at the catalyst surface.

Firstly, this deactivation could be explained considering the mass rate entering into the reactor. At a concentration of 600 ppmv and 200 ml min^{-1} , the reactor receives a load of 10.9 mg of H_2S per hour. Considering that this H_2S is transformed to products, this quantity is sufficient to promote a decrease in the photocatalytic activity. Following the same principle, when working at 217 ppmv of H_2S , after 3 h of operation, a load of 11.8 of H_2S was pumped into the reactor, but interestingly under this situation no catalytic deactivation was observed. Actually, even after 24 h of continuous operation (94.4 mg of H_2S delivered), no inhibition in the catalyst activity was observed. A possible explanation is that at lower concentrations, the system is able to manage low loads by a steady-state of desorption or consumption; a mechanism is not so efficient at high loads.

Another important factor that cannot be ruled out is the effect of the temperature on the deactivation of the catalyst. Adsorption is the first step in the destruction of H_2S on the illuminated surface of the catalyst, a process known to be very dependent upon temperature. Considering that when the light is turned off the working temperature inside the reactor drops from 52°C down to room temperature ($\sim 22^\circ\text{C}$), this effect, although not measured in this work, can potentially alter conversion rates.

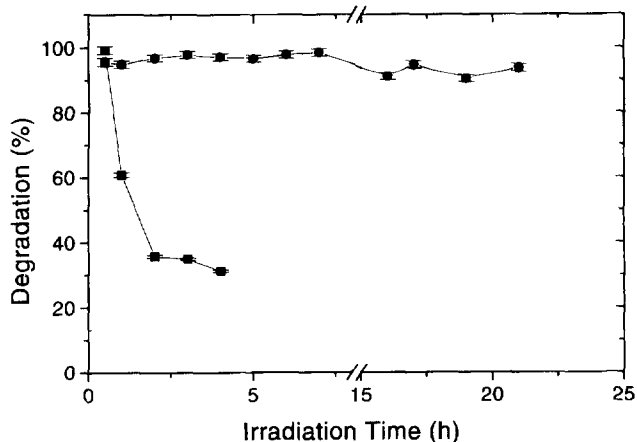


Fig. 5. Photocatalytic activity where: (■) 600 ppmv and (●) 217 ppmv. Experimental conditions: Black-light lamp (30 W), $Q = 200 \text{ ml min}^{-1}$, 80% relative humidity.

3.5. Byproduct adsorption onto the TiO_2 surface

Infrared (IR) studies were carried out to investigate the formation of byproducts on the TiO_2 surface during the irradiation. FTIR spectra of (a) pure TiO_2 , (b) TiO_2 after H_2S adsorption in the dark, and (c) irradiated $\text{TiO}_2/\text{H}_2\text{S}$ are shown in Fig. 6. Infrared spectrum of pure TiO_2 (a) shows strong absorption bands at 3409 and 1637 cm^{-1} , which are typical of adsorbed water on TiO_2 , as already reported in the literature [29]. Most authors agree that molecular water is both strongly and weakly bound, appearing at 1610 – 1640 cm^{-1} (water attached to the catalyst surface), and a number of broad OH stretching bands from water molecules at 3300 – 3500 cm^{-1} . Bands from 3600 to 3800 cm^{-1} are in general assigned to surface-bound hydroxyl groups [30] which have not been observed in this work. The band at 1384 cm^{-1} , appearing in the spectrum of pure TiO_2 as well as in that of the catalyst exposed to H_2S (Fig. 6a and b), probably corresponds to nitrate ions, since during the adsorption step of the catalyst onto the inside wall of the reactor, a suspension of TiO_2 in HNO_3 was used to better fix the powder at the glass surface.

After exposing the catalyst to H_2S for 30 min in the dark (b), one would expect the absorption bands at 2663 cm^{-1} , belonging to H_2S , at 2539 cm^{-1} , corresponding to H_2S molecules hydrogen-bonded to the oxide surface sites, and at 1360 cm^{-1} referring to the bending mode in bound H_2S molecules [30]. However, as shown in Fig. 6b, none of these bands were detected. This behavior can be explained by assuming either a reversible H_2S adsorption onto the catalyst, or that this adsorption does not occur to an extent sufficient to be detected in the IR spectra. When the amount of adsorbed H_2S is normalized by the TiO_2 surface area ($50 \text{ m}^2 \text{ g}^{-1}$), an adsorption density of the $1.06 \times 10^{13} \text{ molecules cm}^{-2}$ was obtained. Values between 10^{13} and $10^{14} \text{ molecules cm}^{-2}$ suggest that relatively few adsorption sites are available at the surface. These results are in agreement with previous findings that the adsorption onto hydroxylated TiO_2 surface

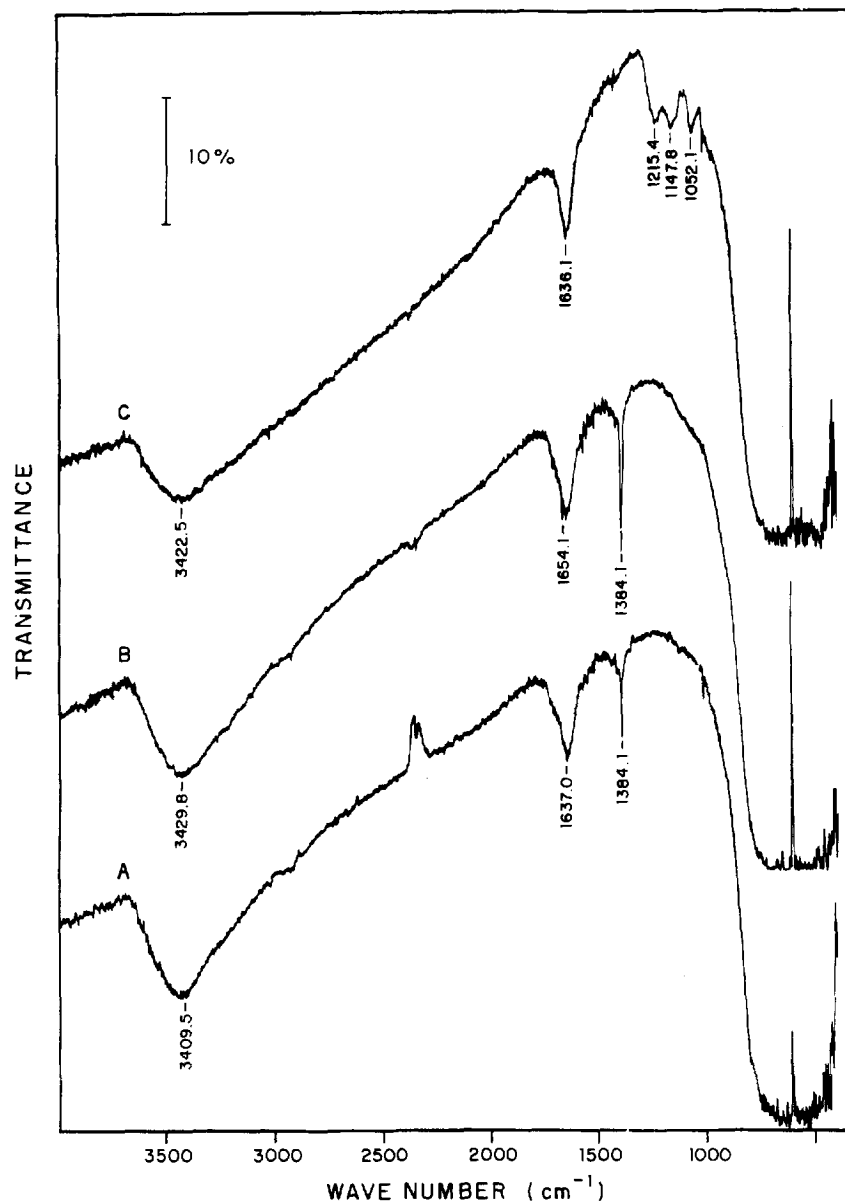


Fig. 6. FTIR spectra of TiO_2 (a) pure, (b) after exposure to H_2S and (c) after exposure to H_2S with irradiation.

does not occur to a large extent in the absence of near-UV illumination [29]. The literature has also shown that nearly perfect TiO_2 surfaces are inert to a variety of gases at room temperature, including H_2S , and that defects on the surface are the major points responsible for gas adsorption.

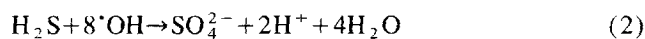
Fig. 6c reveals that three significant spectral changes occur during UV-VIS illumination: (1) nearly complete elimination of the 1384 cm^{-1} band, (2) loss of intensity of the broad band centered near 3420 cm^{-1} , and (3) the appearance of three new bands at 1215 , 1148 , and 1052 cm^{-1} . Result (2) suggests that near-UV illumination leads to two major mechanisms of water consumption: (a) thermal desorption and (b) photocatalytic reaction, which can occur independently at the same time. Change (3) suggests that these bands can be assigned to intermediate surface sulfur oxides, since the

S–O and S=O bonds absorb in the range between 900 and 1500 cm^{-1} [31,32]. Absorption at 1147.2 cm^{-1} is characteristic for sulfate ions, which were detected in low concentration at the outlet of the reactor. The bands observed at 1215 and 1052 cm^{-1} can be attributed to the S(V) intermediates $\text{S}_2\text{O}_6^{-2}$ (1212 cm^{-1}) and $\text{S}_2\text{O}_5^{-2}$ (1052 cm^{-1}), respectively [32].

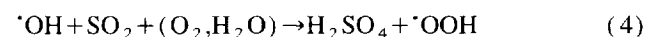
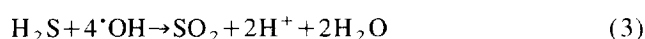
Confirmation that sulfate ions are the major product generated during the photocatalytic destruction of H_2S was obtained by washing the photoreactor with 200 ml of water after 1 h operation, and determining the amount of sulfate in this extract. The mass balance showed that 95% of the total sulfide that entered in the photoreactor was recovered easily as sulfate. The other 4% probably remained strongly attached to the catalyst, since no other compounds were detected in

the final gaseous effluent by using GC/MS. Only 0.02% of the total sulfate was detected in the aqueous trap used to collect the gas stream leaving the photoreactor.

The presence of the SO_4^{2-} ions adsorbed onto TiO_2 can be explained by assuming two different pathways. It can be assumed that $\cdot\text{OH}$ radicals formed on the surface during the illumination are able to oxidize H_2S to H_2SO_4 according to:



An alternative pathway assumes that SO_2 can be produced as an intermediate product, followed by a hydration and oxidation reaction to form H_2SO_4 . In the presence of oxygen and water, the major route to SO_2 formation from H_2S has been proposed by Alloway and Ayres [33]:



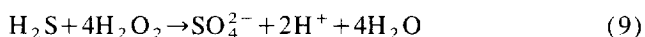
In this work it was not possible to prove which is the preferential route of H_2S oxidation. Although SO_2 can be formed in this process, its quantification is difficult because the kinetic of the reaction (Eq. (4)) is very high.

Sulfur was also the final product observed in the oxidation of H_2S by oxygen when chelated iron absorbent was used as catalyst [34]. Waltrip and Snyder [4] studied hydrogen peroxide addition for the oxidation of H_2S and observed an expected dependence of the final products as a function of pH. According to the authors sulfate was the major ion detected in alkaline conditions, whereas under acidic conditions the major product detected was sulfur.

In this work, elemental sulfur was not detected by FTIR analysis. The presence of S was not detected by changes in catalytic surface color of white to yellow, even after 24 h of continuous operation. Considering the highly oxidizing atmosphere inside the reactor, the following mechanism for the destruction of H_2S at TiO_2 surface is proposed:



Eq. (7) is followed by Eq. (2), then the following:



3.6. Destruction of H_2S stripped from a raw sewage sample

The destruction of H_2S present in a raw sewage sample was tested to evaluate the performance of the reactor when in the presence of possible interferences using real samples. Under the experimental setup described (154 ppmv H_2S at 250 ml min^{-1}) H_2S destruction reached 95% after the steady-state was established (60 min of irradiation). This conversion rate was maintained for 3 h without noticing any inhibition in the catalyst activity, showing that the presence of other

volatile compounds did not impair the performance of the reactor. These results confirm the potential of the process for a wastewater treatment plant for reducing odor nuisance.

4. Conclusion

The gas-phase photocatalytic process using $\text{TiO}_2/\text{UV-VIS}$ showed high efficiency in the destruction of H_2S , reaching degradation yields of 99% at concentration ranges of 33 to 855 ppmv. When working at a 217 ppmv concentration, the photocatalytic activity was maintained over extended operation time. Catalyst deactivation was detected only for concentrations as high as 600 ppmv. The observed inhibition has been attributed to the adsorption of byproducts photoproduced during the oxidation of the parent compound. The main product observed in H_2S oxidation was sulfate ions, which were detected on the TiO_2 surface as well as in the outlet reactor. The process was also tested with the off gas from a raw sewage sample, and the results showed that this process is a viable alternative for the elimination of malodorous compounds present in wastewater treatment plants.

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References

- [1] B. Mills, *Filtration and Separation* 02 (1995) 147.
- [2] M. Tomar, T.H.A. Abdullah, *Water Res.* 28 (1994) 2545.
- [3] C. Bonnin, A. Laborie, H. Paillard, *Water Sci. Tech.* 22 (1990) 65.
- [4] G.D. Waltrip, E.G. Snyder, *J. WPCF* 57 (1985) 1027.
- [5] Metcalf, Eddy, *Wastewater Engineering—Treatment, Disposal and Reuse*, 3rd edn., McGraw-Hill, Singapore, 1991.
- [6] P. Amirhor, G.A. Kuter, M.D. Andrade, *Water Environ. Tech.* 03 (1995) 44.
- [7] M. Lutz, S. Davidson, D. Stowe, *Water Environ. Tech.* 06 (1995) 52.
- [8] L.C.C. Koe, N.C. Tan, *J. Environ. Eng.* 116 (1990) 721.
- [9] F.B. Frechen, *Water Sci. Tech.* 30 (1994) 35.
- [10] J. Peral, D.F. Ollis, *J. Catal.* 136 (1992) 554.
- [11] R. Alberici, W.F. Jardim, Gas-phase destruction of VOCs by heterogeneous photocatalysis, Proceedings of the Sixth International Symposium Chemical Oxidation, Technology for the Nineties, Vanderbilt University, Nashville, TN, April, 1996.
- [12] T.N. Obee, R.T. Brown, *Environ. Sci. Technol.* 29 (1995) 1223.
- [13] R.B. Draper, M.A. Fox, *J. Phys. Chem.* 94 (1990) 4628.
- [14] S.N. Frank, A.J. Bard, *J. Phys. Chem.* 81 (1977) 1484.
- [15] A.P. Hong, D.W. Bahnemann, M.R. Hoffmann, *J. Phys. Chem.* 91 (1987) 6245.
- [16] K. Suzuki, S. Satoh, T. Yoshida, *Denki Kagaku* 59 (1991) 521.
- [17] W.F. Jardim, C.P. Huang, Gas-phase photocatalytic destruction of H_2S using UV/ TiO_2 , Proceedings of the Sixth International Symposium Chemical Oxidation, Technology for the Nineties, Vanderbilt University, Nashville, TN, April 15–17, 1996.

- [18] J. Calvert, J. Pitts, *Photochemistry*, Wiley, New York, 1966.
- [19] A.S. Greenberg, L.S. Clesceri, A.D. Eaton (Eds.), *Standard Methods for the Examination of Water and Wastewater*, 18th edn., American Public Health Association, Washington, DC, 1992, p. 4126.
- [20] G. Lu, A.L. Linsebigler, J.T. Jr. Yates, *J. Phys. Chem.* 99 (1995) 7626.
- [21] G. Lu, A.L. Linsebigler, J.T. Jr. Yates, *J. Phys. Chem.* 102 (1995) 4657.
- [22] J.C.S. Wong, A.L. Linsebigler, G. Lu, J. Fan, J.T. Jr. Yates, *J. Phys. Chem.* 99 (1995) 335.
- [23] H. Gerischer, A. Heller, *J. Phys. Chem.* 95 (1991) 5261.
- [24] U. Stafford, K.A. Gray, P.V. Kamat, A. Varma, *Chem. Phys. Lett.* 205 (1993) 55.
- [25] A.P. Hong, D.W. Bahnemann, M.R. Hoffmann, *J. Phys. Chem.* 91 (1987) 6245.
- [26] R.B. Drapper, M.A. Fox, *Langmuir* 6 (1990) 1396.
- [27] C.G. Hill Jr., *An Introduction to Chemical Engineering Kinetics & Reactor Design*, Wiley, New York, 1977.
- [28] H.V. Langenhove, K. Roelstaete, N. Shamp, J. Houtmeyers, *Water Res.* 19 (1985) 597.
- [29] L.A. Phillips, G.B. Raupp, *J. Mol. Catal.* 77 (1992) 297.
- [30] D.D. Beck, J.M. White, C.T. Ratcliffe, *J. Phys. Chem.* 90 (1986) 3123.
- [31] K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, Wiley, Toronto, 1970.
- [32] K. Buijs, *J. Inorg. Nucl. Chem.* 24 (1962) 229.
- [33] B.J. Alloway, D.C. Ayres, *Chemical Principles of Environmental Pollution*, Chapman & Hall, Oxford, 1993.
- [34] L.A. Mansfield, P.B. Melnyk, G.C. Richardson, *Water Environ. Res.* 64 (1992) 120.