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Photocatalytic Purification of Wastewater Polluted by Odorant Sulfur Compounds Using Titanium Oxide in a Continuous Photoreactor

Abstract: Using titanium dioxide, photocatalytic degradation of waste water polluted by commercial mercaptans (80% *t*-butyl mercaptan and 20% methyl ethyl sulfide) was investigated in a continuous photoreactor in the presence of UV irradiation. The reaction was performed at different pH of solution, intensity of irradiation, and initial concentration of odorant. Kinetics and mechanism of photocatalytic decomposition of mercaptans were studied by *ex situ* FTIR measurements of intermediates. The results showed that the photocatalytic process for degradation of mercaptans was an efficient method for mineralization of sulfur odorants in waste water. A proposed mechanism of mineralization of mercaptan was presented based on the results.

Keywords: mercaptan, titanium oxide, photocatalyst, odorant, mineralization

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1 Introduction

Volatile sulfur compounds such as mercaptans are highly toxic and have obnoxious odor and extremely low odor threshold. They are known to be produced in aerobic or anaerobic conditions from natural sources, petroleum refining processes, gas refineries, wood pulping industry, sewage treatment, and energy-related activities. Oxidation of these compounds in atmospheric conditions leads to formation of SO₂, which eventually becomes the main compound responsible for acid rains.

One of the industrial sources of mercaptan emission is city gas station (CGS) which includes the injection systems of mercaptan from storage to the natural gas stream for odorization of it. The main environmental problem of these units is the residual mercaptan in the storage which causes the emission of mercaptan in environment thus leading to pollution [1]. In the North of Iran, about 500 storages of mercaptan have been consumed in 2012. At least 1,000 ml of mercaptan remains in each storage after consuming of it which can be emitted in the environment.

The common technologies that are evaluated for removing mercaptan include the following, as noted by Kastner and Das [2]:

- Oxidation
 - Catalytic
 - Chemical
 - UV/ozone oxidation
 - Heterogeneous photocatalysis
- Adsorption with adsorbent materials such as activated carbon and zeolite
- Other commercial technologies
 - Absorption by amines
 - Incineration

Chemical oxidation of mercaptans includes its reaction with the chemical oxidants such as hypochlorite which eliminates its odor but limits the pollution caused by the oxidation of mercaptan to corresponding alkyl sulfonates that are poorly biodegradable [3].

Adsorption is one of the most widely applied control technologies for volatile sulfur compounds. In this process, mercaptans are collected on the surface of a porous solid. Activated carbon is by far the adsorbent most often used for low organic gas concentrations because of its high ability to absorption [4]. However, it is only used for treatment of gaseous streams and absorption of light mercaptans such as methyl mercaptan (MM) and ethyl mercaptan.

Catalytic oxidation is used for removing mercaptans from naphtha in the petroleum refinery, which is called

Merox process. Cobalt phthalocyanine is the catalyst of Merox unit which operates in the presence of caustic solution. This is an efficient process, but the catalyst is very expensive.

Titanium dioxide as the photocatalyst has proved a high activity in the photocatalytic oxidation of various organic compounds. The complete oxidation of organic compounds to CO_2 , H_2O , and inorganic constituents is called “mineralization” of toxic and non-biodegradable organics. During past two decades, some papers have been published about the photocatalytic oxidation of mercaptans. Low et al. [5] studied the photooxidation of some derivatives of mercaptans and amines. They found that the degradation of these compounds in the presence of TiO_2 led to produce the nitrated and sulfated compounds. Mineralization of some cyclic mercaptans by titanium dioxide was performed by Habibi et al. [6]. Guillard et al. [7], and Liu et al. [8] used TiO_2 for degradation of light malodorous compounds such as MMs and dimethyl disulfide, respectively. Photocatalytic oxidation of dibenzothiophene in the crude oil by Huang et al. [9] has been attracted as an alternative new method for oxidative desulfurization of light oils instead of hydrodesulfurization because of lower temperature, pressure, and cost of operation.

In this study, we investigate the photocatalytic oxidation and mineralization of residual mercaptan in their storages which are used for odorization of natural gas stream in CGSs. The effects of pH, UV intensity, concentration of mercaptans, and time of reaction on the photocatalytic oxidation of mercaptan are studied. Finally, a

mechanism of photodegradation of *t*-butyl mercaptan (TBM), as the main component of commercial natural gas odorant, is presented.

2 Experimental

2.1 Chemicals

TBM as the main component of commercial mercaptan for natural gas odorization was provided by Merck, Germany (<99%). Commercial mercaptan (80% TBM and 20% methyl ethyl sulfide) was kindly provided by Arkema Company, USA. Ultrapure water was used for preparation of the stock solutions and filtered through a Milli-Q PLUS 185 water system (Millipore, Bedford, MA). Organic solvents were not used to minimize any co-solvent effects on the photodegradation. Titanium dioxide used was TiO_2 Degussa P25 (anatase/rutile = 80/20, surface area = $51 \text{ m}^2 \text{ g}^{-1}$, and average particle size = 21 nm) as a commercial photocatalyst.

2.2 Photoreactor and light source

A cylindrical photocatalytic reactor was made by glass (Pyrex, USA) with 10 cm of internal diameter and 80 cm of height and used in vertical conditions. A schematic diagram of the experimental set-up is presented in

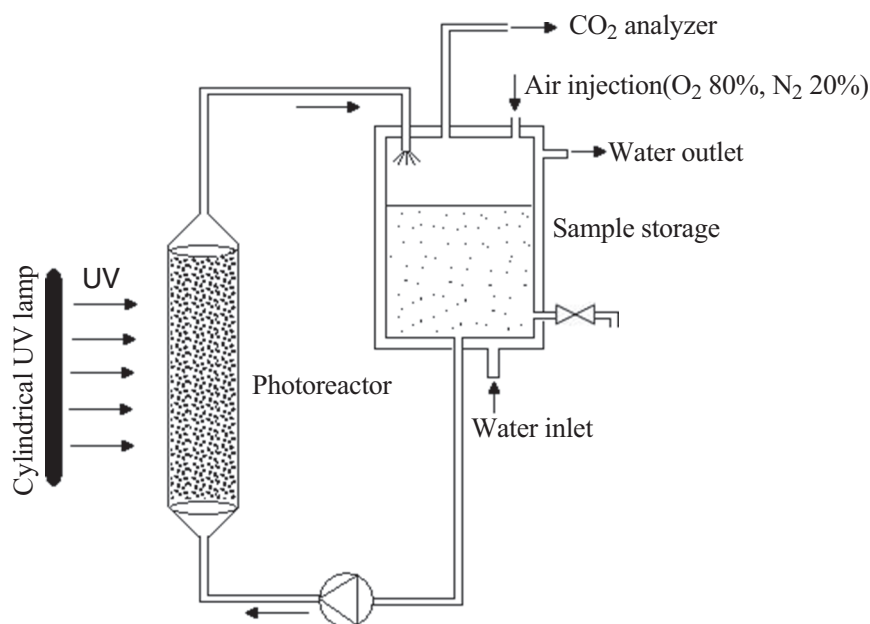


Figure 1 Schematic diagram of photoreactor process

Figure 1. Two sinter glass filters (mesh 4) prevented the catalyst consumption. The cylindrical high-pressure mercury lamp (Philips 120 W, Holland), emitting 21.7 mW cm^{-2} at 365 nm, was used as UV source, and distance between the lamp and the photoreactor was changed according to desired intensity of emission. Mercaptan solution was introduced from bottom to top of the reactor. Flow rate was adjusted for prevention of sedimentation of particles. So the particles of photocatalyst were floated in the reactor, while the concentration of photocatalyst and reactant was similar according to the analysis of composition of solution in different parts of the reactor.

In all experiments, the temperature of photoreactor was kept at $25 \pm 2^\circ\text{C}$ by a water jacket and a thermostat to prevent the temperature increase and evaporation of mercaptans.

2.3 Experimental procedure

Photocatalytic oxidation of mercaptan was performed by use of a suspension of desired amount of photocatalyst powder into 10 l of aqueous solution of commercial mercaptan. A solution containing 5 g l^{-1} (5,000 ppm) of mercaptan was prepared and diluted to desired concentration of it. The suspension was circulated by a micro-pump (Discharge = 10 l s^{-1} , Head = 10 m). Sampling was done at different times of reaction. Before analysis, each sample was centrifuged in order to remove any possible particles of TiO_2 . For study of pH effect, sodium hypochlorite (5%) was added to obtain the desired pH of solution.

2.4 Analysis and kinetic study

Since the photocatalytic reactions can mineralize organic samples and convert them to CO_2 and H_2O , the residual organic components can be analyzed by determination of total organic compound (TOC). So the decrease of mercaptan concentration during photolysis and photocatalysis, as well as the concomitant evolution of degradation products, was followed by direct injection of aqueous samples into the total organic carbon (TOC) analyzer (ANATOC SGE, Australia). For calculation of carbon balance before and after photocatalytic reactions, the concentration of CO_2 was determined by use of an aqueous solution saturated with $\text{Ba}(\text{OH})_2$ in which the gases exiting from the photoreactor were bubbled, and total amount of $\text{BaCO}_3(\text{s})$ was determined.

Kinetics of photocatalytic degradation was studied according to the Langmuir–Hinshelwood mechanism.

$$r = k\theta = kKC/1 + KC \quad (1)$$

where k is the apparent rate constant which includes various parameters such as weight of the catalyst and intensity of light, and K is adsorption constant. Since the initial concentration C_0 is low, KC in the denominator can be neglected and the rate becomes first order:

$$r = -dC/dt = kKC = k_a C \quad (2)$$

where k_a is global apparent rate constant of pseudo-first order. Integral form $C = f(t)$ of the rate equation is

$$\ln C_0/C = k_a t \quad (3)$$

The global apparent rate constant k_a is used to evaluate the photocatalytic activity. Similar description can be used for extraction of zero- and pseudo-second-order relations:

$$C_0 - C = -k_a t \quad (4)$$

$$1/C - 1/C_0 = k_a t \quad (5)$$

For determination of possible reaction pathways, 25 mg of P25 was added to 25 cc of TBM and stirred under UV irradiation (4 mW cm^{-2}). The sampling was performed at the times of 30, 60, 90, 120, and 180 min after reaction. Each sample was centrifuged, and the intermediates were identified by means of *ex situ* FTIR spectrophotometer (Bruker, Germany).

3 Results and discussion

Figure 2 shows removal of TOC by increase of reaction time at different initial concentrations of mercaptan in the photocatalytic reactor.

In the sample containing 500 ppm of mercaptan, the total amount of removing TOC after 180 min is near to 97%. The percentages of TOC removal for initial concentrations of 1,000, 2,000, 3,000, and 5,000 ppm are 93, 91, 90, and 85, respectively. Calculation of carbon balance showed that the evaporation of mercaptan was not occurred.

Table 1 shows the results of kinetic study after fitting of the obtained results by use of the kinetic models. It can be seen that the photocatalytic degradation of mercaptan is kinetically a first-order reaction. The rate constants are between 2.34×10^{-2} and $1.12 \times 10^{-2} \text{ min}^{-1}$.

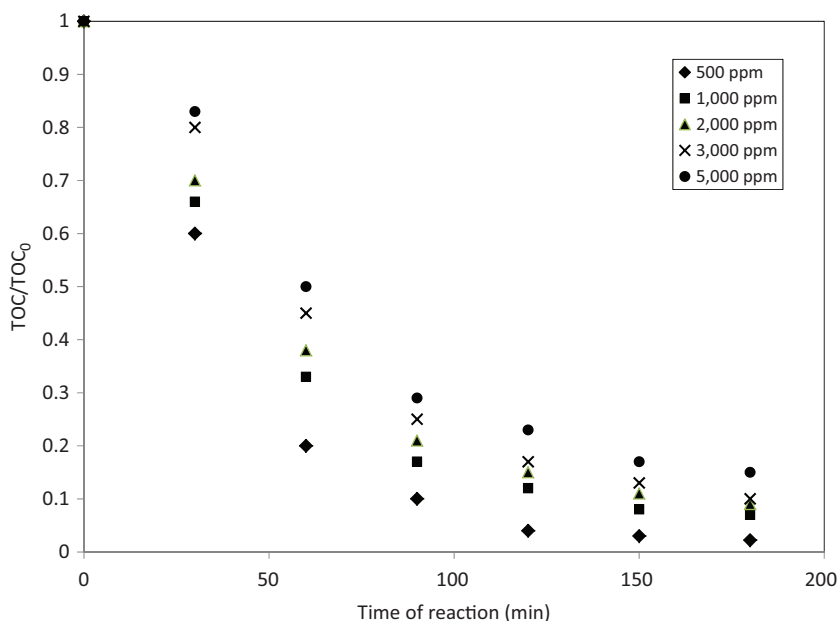


Figure 2 TOC removal vs time of reaction ($\text{pH} = 7$, $I = 4 \text{ mW cm}^{-2}$, $C_{\text{TiO}_2} = 1 \text{ g l}^{-1}$)

Table 1 Kinetic parameters photodecomposition of commercial mercaptans

Concentration (ppm)	k_1 (min^{-1})	R^2	k_2 ($\text{l mg}^{-1} \text{ min}^{-1}$)	R^2	k_0 ($\text{mg l}^{-1} \text{ min}^{-1}$)	R^2
500	2.34×10^{-2}	0.988	4.10×10^{-4}	0.835	3.527	0.582
1,000	1.65×10^{-2}	0.986	6.80×10^{-5}	0.900	6.545	0.695
2,000	1.47×10^{-2}	0.983	2.54×10^{-5}	0.916	12.615	0.748
3,000	1.36×10^{-2}	0.977	1.45×10^{-5}	0.904	18.264	0.814
5,000	1.12×10^{-2}	0.961	5.96×10^{-6}	0.925	28.626	0.852

Notes: k_1 : rate constant of eq. (3), k_0 : rate constant of eq. (4), and k_2 : rate constant of eq. (5)

Figure 3 shows the percentage of TOC removal in different concentrations of photocatalyst. It can be seen that for concentration greater than 1 g l^{-1} , the percentage of TOC removal is higher than 90. This is a result of the increase in photoabsorption by particles of TiO_2 which increases the production of free electrons and holes and consequently photoreaction rates.

Figure 4 shows the effect of light intensity of UV irradiation on the photocatalytic activity. It is well known that the balance of light emission and adsorption of photon by particles of TiO_2 is an effective parameter on activity [8]. In low intensities, the excitation of electron on the external surface of TiO_2 particles is decreased. By increase of UV intensity, the photoelectrons are increased and the reaction rate is increased.

Effect of pH on TOC removal is presented in Figure 5. These results are similar to those of the previous works on the other mercaptans [6, 10]. The role

of pH on the efficiency of removing mercaptan is related to the influence on the adsorption of mercaptan molecules onto the TiO_2 surfaces, as an important step for the photocatalytic degradation. Moreover, hydroxyl radicals can be formed by the reaction between hydroxide ions and positive holes. The positive holes are considered as the major oxidation species at low pH, whereas hydroxyl radicals are considered as the predominant species at the neutral or high pH levels, but in very alkaline solution there is a Columbic repulsion between the negatively charged surface of photocatalyst and the hydroxide anions which can prevent the formation of hydroxyl radicals, thus the efficiency of the process is logically enhanced.

Analysis of *ex situ* FTIR measurements is shown in Figures 6. In spectrum (a), there are two weak peaks at $1,000\text{--}1,300 \text{ cm}^{-1}$ and $2,900$ which are corresponded to the stretching bands of C–H and S–H bonds of TBM,

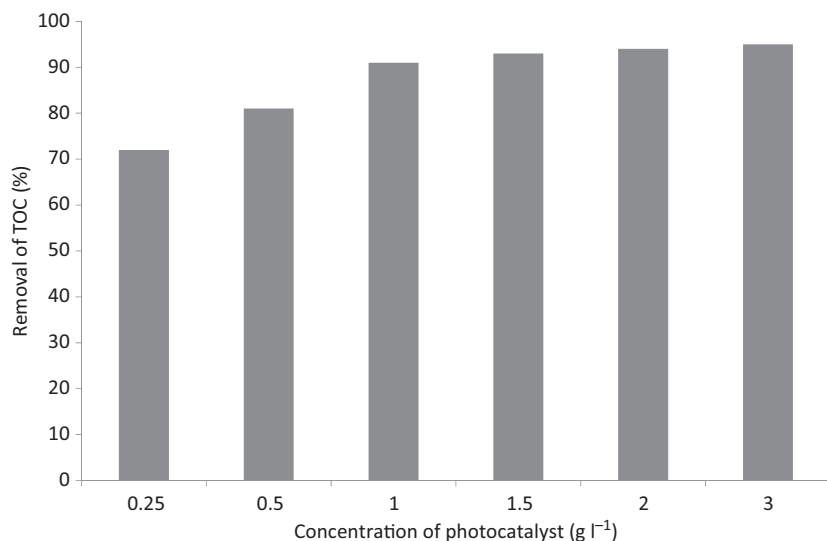


Figure 3 TOC removal vs concentration of TiO₂ (pH = 7, I = 4 mW cm⁻², C_{mercaptan} = 1,000 mg l⁻¹)

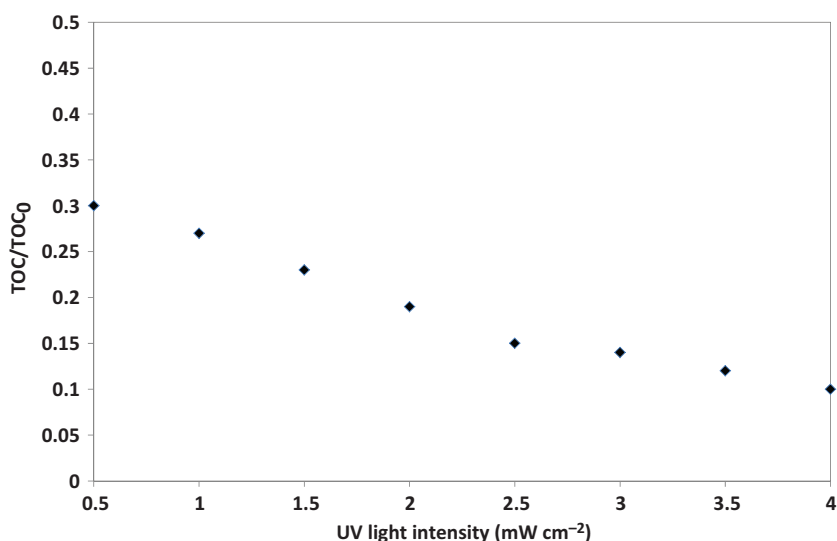
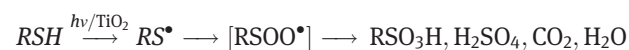


Figure 4 TOC removal vs light intensity (pH = 7, C_{mercaptan} = 1,000 mg l⁻¹, C_{TiO₂} = 1 g l⁻¹)

respectively. By developing the photoreactions, it is observed two new peaks at 1,150 and 1,300 cm⁻¹ which are corresponded to the symmetric and asymmetric stretchings of S=O group in sulfonates, sulfates, and sulfonic acids, respectively (spectrums b–d). Moreover, we can see a broad peak in the range of 3,000–3,600 and 1,600–1,700 cm⁻¹ which can be indicated the presence of water as a main product of photocatalytic degradation of TBM. The area of these bands increases with the time of reaction.

This is an evidence of the mechanism which is proposed by Canela et al. [11] with the parallel reactions for

positive holes and hydroxyl radicals which is conducted by electron transferring to an adsorbed hydroxyl radical or hole trapping by an adsorbed sulfur-containing compounds, sulfonic and sulfuric acids.



Sodium hypochlorite as an oxidation reagent creates a synergetic effect for mercaptan oxidation. In the presence of water, the mechanism is involved sulfurane-type intermediates, and the yield of sulfuric acid formation is increased which can be neutralized by sodium hypochlorite in solution.

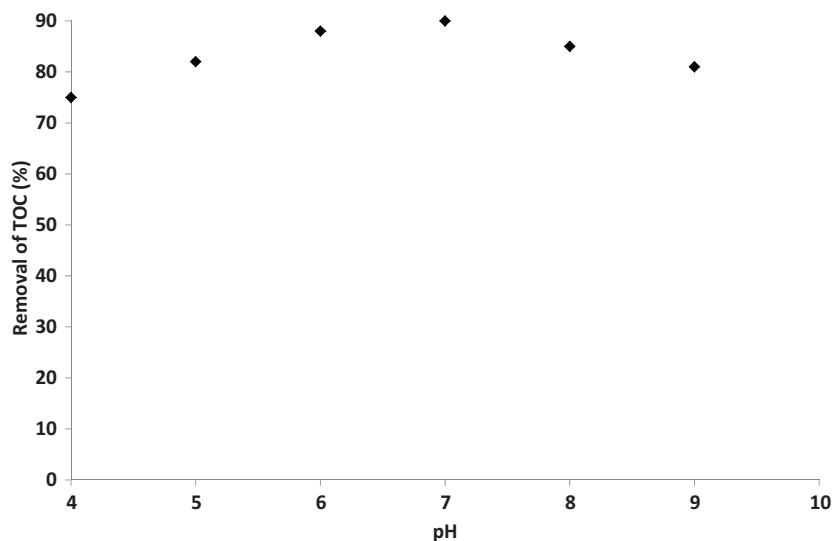


Figure 5 Effect of pH on the TOC removal ($I = 4 \text{ mW cm}^{-2}$, $C_{\text{TiO}_2} = 1 \text{ g l}^{-1}$, $C_{\text{mercaptan}} = 1,000 \text{ mg l}^{-1}$)

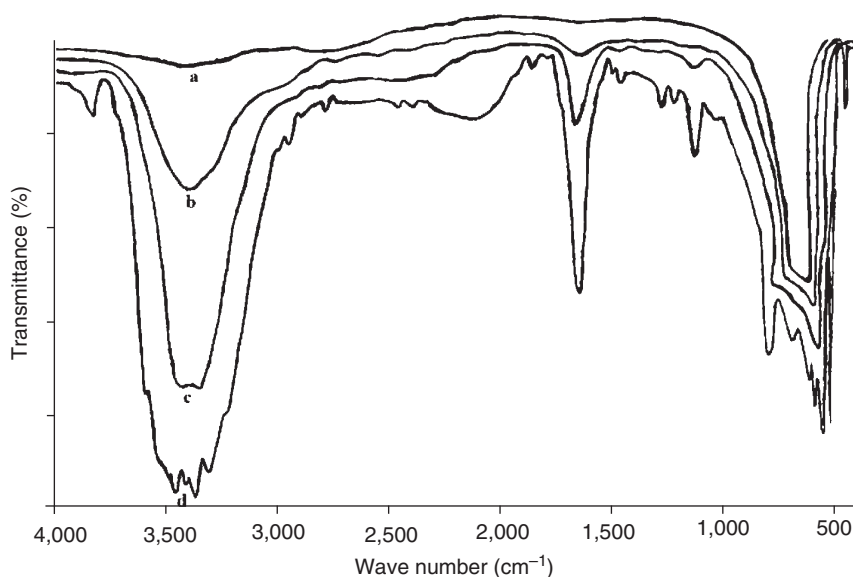


Figure 6 FTIR spectrums of samples: a: after 30 min, b: after 60 min, c: after 90 min, and d: after 120 min

4 Conclusions

Photocatalytic degradation of commercial mercaptan as an odorous compound is a very effective method for mineralization of it. By use of hypochlorite, mercaptan is converted to the corresponding alkyl sulfonate salts, and the deodorization of mercaptan and prevention of odor emission in operation unit can be effectively obtained. Using commercial titanium dioxide (Degussa)

as the photocatalyst with the concentration of 1 g l^{-1} , organic compounds of solution can be almost mineralized in the presence of UV irradiation in pH ranges between 5 and 9. Analysis of kinetic parameters shows that the reaction is performed as a first-order reaction. Study of the chemical structure of products gives an evidence of Canela's mechanism by production of sulf-oxide and sulfone radicals which are converted to CO_2 , H_2O , and sulfate salts.

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