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Journal of Photochemistry and Photobiology A: Chemistry 174 (2005) 45–52

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

Photocatalytic degradation of some organic sulfides as environmental pollutants using titanium dioxide suspension

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Received 15 September 2004; received in revised form 22 December 2004; accepted 23 February 2005

Abstract

The photocatalytic degradation of four organic sulfide compounds containing different functionalities; methyl phenyl sulfide (MPS), methyl benzimidazoyl sulfide (MBS), propyl benzimidazoyl sulfide (PBS) and 3-propenyl benzimidazoyl sulfide (3-PBS) as environmental pollutants using TiO_2 photocatalyst suspension under UV-light irradiation in aqueous and organic (ethanol, methanol, acetonitrile, CCl_4 and *n*-hexane) solvents was studied. The effect of important operational parameters such as solvent, catalyst loading, oxygen flow, irradiation time, pH, and comparison of photocatalytic activity with different commercial ZnO and TiO_2 (rutile and anatase) catalysts were also studied. The photodegradation rate was determined for each experiment and the following trend viz. TiO_2 (rutile) > ZnO > TiO_2 (anatase) was observed, suggesting that ZnO absorbs a large fraction of the UV-light and absorbs more light quanta than TiO_2 (anatase). The effectiveness of large particles in this reaction is understandable from the properties of TiO_2 particles, which indicate that band bending is necessary to oxidize sulfide compounds. To develop the band bending in particles, their size and donor density are important. Usually, rutile powders have larger particle sizes than the anatase powders, because they are produced at higher temperature, and thus are advantageous for band bending. Results show that the photocatalytic degradation is well progressed in the aqueous solution and in the presence of oxygen. Optimum value of TiO_2 (rutile) photocatalyst was obtained 30 mg per 20 ml of solution. The best UV-light irradiation time for MPS was 100 min and for the other sulfide compounds was 3 h. Further studies showed that the optimum values of solution pH were observed 8 and 6 for MPS and for the others, respectively. The complete mineralization was confirmed by total organic carbon (TOC) analysis and estimation of the formation of inorganic ions such as NH_4^+, CO_2 and SO_4^{2-}.

Keywords: Photocatalytic degradation; Desulfurization; Methyl phenyl sulfide; Methyl benzimidazoyl sulfide; Propyl benzimidazoyl sulfide; 3-Propenyl benzimidazoyl sulfide

1. Introduction

Reduced sulfur compounds such as sulfides, disulfides and mercaptans are the by-products of industrial processes and are known as waste, natural waters and the earth's atmosphere pollutants [1–3]. The spontaneous oxidation of these sulfides leads to formation of tropospheric SO_2, which is eventually converted into H_2SO_4, one of the main components in acidic rains through the reaction with atmosphere humidity [4]. On the other hand, reduced organic sulfur compounds are mostly released in anaerobic biological activities. Sewage and industrial wastewater treatment plants and fermentation treatment of animal feces in livestock industry are examples of places where pronounced anthropogenic generation of these compounds can be observed [5–7]. Since the smells of these organic sulfides are often unpleasant for human life their odor treatment is important. Currently applied methods of odor removal are biofiltration, bioscrubbing, activated carbon adsorption, wet chemical scrubbing, thermal oxidation, water hydrolysis by aqueous alkalis, perhydrolysis and oxidative chlorination [8–12]. Each of these methods has its own advantages, but all of them have one common disadvantage such as large volumes of degassing solutions

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doi:10.1016/j.jphotochem.2005.02.012

or toxic gaseous derivatives, which require further treatment [13]. A new and highly promising universal method for the destruction of various airborne and dissolved organics is photocatalytic oxidation [14]. Among metal oxides used as the photocatalyst for environmental clean up, titanium dioxide (TiO_2) is one of the most promising materials because of its stability and nontoxicity [15–20]. When TiO_2 is irradiated by UV photons with energy higher than its band gap (ca. 3.2 eV for anatase), electron–hole pairs are generated. These charge carriers can migrate to the semiconductor surface to initiate redox reactions with adsorbents. However, the mechanism of photoxidation on the TiO_2 surface is still under discussion [21–28]. It is proposed that the surface hydroxyl groups react with the holes to form the surface-bound OH radicals, which then oxidize the surface adsorbents. Support for this mechanism comes from the chemical identification of the hydroxylated oxidation intermediates, EPR detection of the surface OH radical in aqueous TiO_2 sols, the scavenging OH radicals, and the kinetic isotope effect [29–32]. Several researchers also reported that the surface-bound OH radicals are key species for oxidation reaction because the diffusion of surface-bound OH radicals from the TiO_2 surface into the bulk solution is minimal [32,33].

Recently, we have reported heterogeneous photocatalytic mineralization of some thiols on the Degussa P25 TiO_2 [34,35] and some cyclic saturated amines on the ZnO photocatalyst [36]. It is well known that the photocatalyst nature and solvent plays crucial roles in the reaction course. But to the best of our knowledge from literature, less attention has been paid to the comparison of photocatalytic activity of different commercial ZnO and TiO_2 (rutile and anatase) catalysts for degradation of organic sulfide compounds under UV-light in the aqueous and organic solvents. Therefore, in the present work we have investigated the effect of important operational parameters (including solvent, type of catalyst, amount of catalyst, illumination time of UV-light, pH and presence of molecular oxygen) on the photocatalytic degradation of methyl phenyl sulfide (MPS), methyl benzimidazoyl sulfide (MBS), poropyl benzimidazoyl sulfide (PBS) and 3-propeny benzimidazoyl sulfide (3-PBS) as a model molecules of organic pollutant to optimization the process for practical applications.

2. Experiments

2.1. Materials

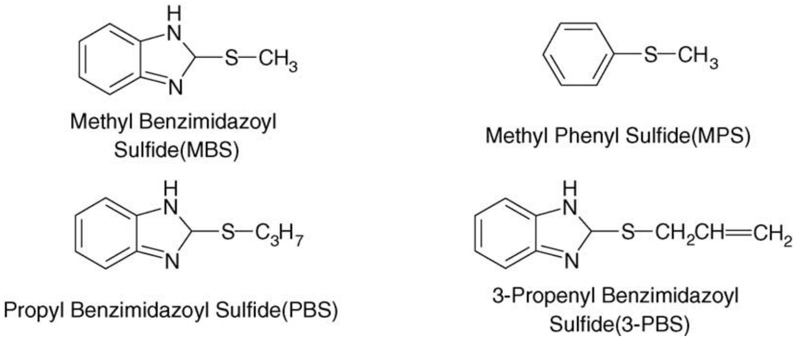
The analytical grade anatase and rutile TiO_2 powders with the BET surface area of 48 and 22 $m^2\,g^{-1}$, respectively were obtained from Aldrich. ZnO, methyl phenyl sulfide (MPS) and all solvents (ethanol, methanol, acetonitrile, CCl_4 and *n*-hexane) were prepared from Merck and used without further purification. Methyl benzimidazoyl sulfide (MBS), poropyl benzimidazoyl sulfide (PBS) and 3-propeny benzimidazoyl sulfide (3-PBS) were synthesized and purified according to the previous reports [37]. The molecular chemical structure of these sulfides is shown in Scheme 1. The pH of solution was adjusted using diluted aqueous buffers that were prepared by the following compounds: KH_2PO_4, Na_2HPO_4, NaOAC, HOAC, $Na_2B_4O_7$, HCl and NaOH. In all experiments doubly distilled water was used.

2.2. Experiments equipment

Aqueous solutions of sulfide compounds were irradiated in a Pyrex tubular reactor. A magnetic stirrer was placed under the reactor. A 400 W high-pressure mercury lamp was used as the UV-light source. Oxygen was introduced to the solution from a gas cylinder at a flow rate of 5 ml/min through a needle valve. The Pyrex reactor was uniformly illuminated and its temperature kept constant at 25 °C by a water jacket and thermostat. The set up of the photocatalytic degradation experiments is shown in Fig. 1. The concentration of organic sulfides was monitored by periodic sampling during the course of experiments using a double beam Shimadzu 160 UV–vis spectrophotometer. The pH measurements were done using a Metrohm 620 pH meter. A Hettich EBA 85 centrifuge was used to separate photocatalyst from sample solution. The total organic carbon (TOC) was measured using a Beckman 915A total organic carbon analyzer.

2.3. Photoirradiation and analysis procedure

In each experiment 20 ml of MPS (50 ppm), MBS, PBS or 3-PBS (25 ppm) solutions was used. Reasons for choos-



Scheme 1. Molecular structure of selected organic sulfides.

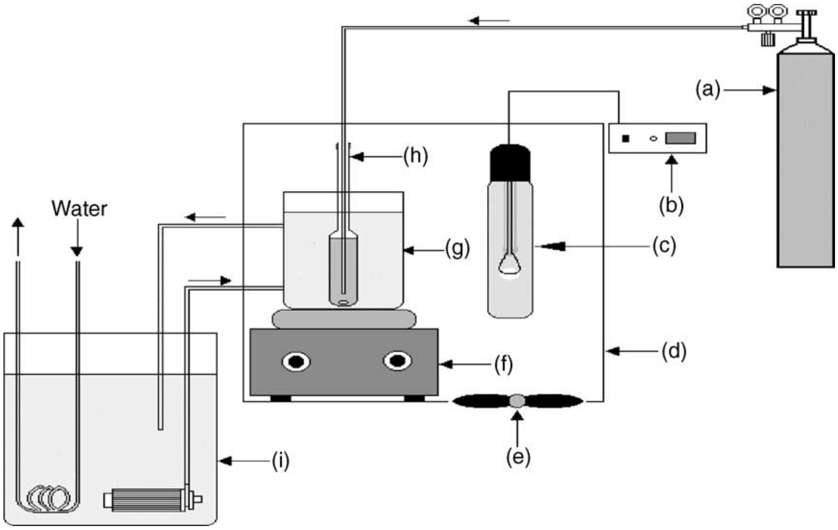


Fig. 1. Photocatalytic degradation set up: (a) oxygen cylinder; (b) power supply; (c) 400 W high-pressure Hg lamp; (d) photoreactor with aluminum foil as reflector for a full irradiation of catalyst; (e) fan; (f) magnetic stirrer; (g) 2 l Pyrex beaker; (h) photocatalytic degradation cell; (i) water thermostat hake model f-122.

ing these concentrations are less solubility in water and long degradation time for MBS, PBS and 3-PBS with respect to MPS. All procedures for the sample preparation were preformed with shielding from the UV-light. The photocatalyst powders were suspended in the test solutions. Then, the solutions were irradiated with and without continuous bubbling of oxygen under vigorous stirring. After a significant irradiation time which depended on the nature of sulfide compounds, TiO_2 or ZnO photocatalysts were completely removed by centrifugation, and solution was filtered through a Millipore filter (pore size 0.22 μm) for the following UV absorption measurements. The concentration changes of sulfide compounds were followed by monitoring their absorption peaks at $\lambda_{max} = 252$, 282, 282.8 and 283 nm for MPS, MBS, PBS and 3-PBS, respectively.

The initial solution of each organic sulfide was used as a standard. The SO_4^{2-} concentration as one of the photodegradation products in aqueous solution was determined by adding 9.5 ml of solution containing 0–10 mmol of sulfate to 0.5 ml of developer solution which contains NaCl 75 g; ethanol 100 ml; concentrated HCl 30 ml; glycerol 50 ml and distilled water 300 ml. To this mixture $BaCl_2$ 0.05 g was added and the solution was stirred thoroughly for 1 min. The stabilized turbidity of $BaSO_4$ suspension in the developer solution was measured at 540 nm.

The ammonia concentration in aqueous solution was also determined spectrophotometrically at $\lambda_{max} = 410$ nm in the presence of Nessler's reagent. The formation of CO_2 was detected as $BaCO_3$(s) that separated in the aqueous solution that saturated with $Ba(OH)_2$ in which the gases exiting from the reactor bubbled.

3. Results and discussion

According to Gilbert and Mercier [38], the main factors affecting degradability of organic compounds are (i) reagent solubility, (ii) solution polarity, (iii) reactivity or acido-basicity of solvent, and (iv) competitive chemisorption of substrates, products and solvent on the surface of catalyst. Therefore, the physico-chemical properties of organic sulfides must directly affect their photocatalytic degradability. We will discuss the parameters on which mentioned factors depend in this section.

3.1. *Effect of photocatalyst type on the degradation of MPS and MBS*

The effect of photocatalyst type on the photocatalytic degradation of MPS and MBS aqueous solutions was investigated. Results (Fig. 2) show that the order of photocatalytic activity is as follows: TiO_2 (rutile) > ZnO > TiO_2 (anatase). As a result, to obtain efficient photocatalytic degradation, many structural parameters of photocatalyst such as particle size, crystalline quality, morphology, specific surface area, surface state, appropriate phase structure, texture and electronic properties, etc. are important. A lack of one of these conditions leads to the sharp reduction of activity of photocatalyst.

The reason for greater activity of ZnO compared with TiO_2 (anatase) is due to the absorption of more light quanta by ZnO than TiO_2 (anatase). Since the band gap of ZnO is 3.17 eV, the quantum efficiency of ZnO powder is significantly larger than the TiO_2 Degussa P25 (70% anatase and 30% rutile) and hence higher efficiencies have been reported for ZnO [39]. The greatest advantage of ZnO is

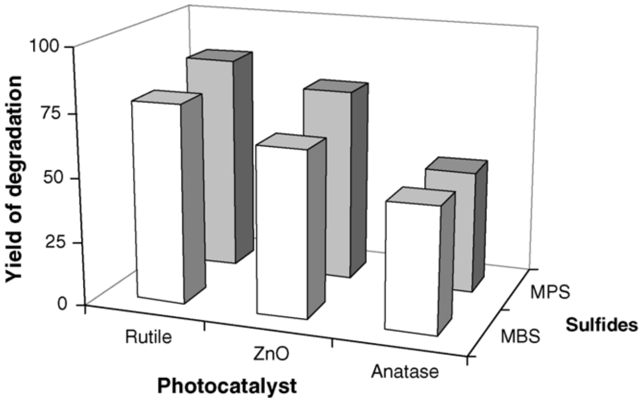


Fig. 2. Percent of photocatalytic degradation of MPS and MBS in the presence of three photocatalysts under UV-irradiation time 1.5 and 3 h for MPS and MBS, respectively and flux of O_2; 5 ml/min; room temperature.

that it absorbs a large fraction of the solar spectrum than TiO_2.

The high activity trend for TiO_2 (rutile) compared with TiO_2 (anatase) can be explained based on this fact that anatase particles have small sizes and high active surface area that their large surface area is especially effective for capturing low concentration chemicals. In addition, the large band gap of anatase has been considered to be related to its high activity. However, in photodegradation of sulfide compounds, we have found that rutile particles with large particle sizes are more active than the anatase particles. The effectiveness of large particles in this reaction is understandable from the properties of TiO_2 particles, which indicate that band bending is necessary to oxidize sulfide compounds. To develop the band bending in particles, their size and donor density are important. For example, if the donor density is about $3 \times 10^{17}\ \mathrm{cm}^{-3}$, a space charge layer of 100 nm is necessary to develop a potential drop of 0.3 eV. Usually, rutile powders have larger particle sizes than the anatase powders because they are produced at higher temperatures, and thus are advantageous for band bending [40]. It should be stressed that in the next experiments, we used the TiO_2 (rutile) as photocatalyst unless elsewhere stated.

3.2. *Effect of solvent on the degradation of MPS and MBS*

Table 1 shows the photocatalytic degradation of MPS and MBS in various solvents. As shown in this table, the solvent plays a crucial role on reaction course. From our findings among these solvents, water was the best media for photocatalytic degradation of these sulfide compounds. In general, it is well known that the TiO_2 photocatalytic reactions in aqueous solution proceed mainly by the contributions of active oxygen species, such as $^{\bullet}OH$, $O_2^{\bullet -}$ and H_2O_2. These species are formed by Eqs. (1)–(7), where e^- represents photoinduced conduction band electrons. The photoinduced valence band holes are trapped at the surface of TiO_2 forming trapped holes. Since, the reaction ability of $^{\bullet}OH$ is high enough to attack any organic molecules, it has been assigned as a key species in the mineralization mechanism of many hazardous chemical compounds. Therefore, discrepancy between the percent of photocatalytic degradation of sulfide compounds may be due to the ability of their direct hole capturing and/or photocatalytic degradation mechanisms [41].

Table 1
Photocatalytic degradation percent of MPS and MBS in several solvents: TiO_2 (rutile) 30 mg; irradiation time 1.5 and 3 h for MPS and MBS, respectively; 5 ml/min flux of O_2; room temperature

Solvent	Polarity	MPS degradation	MBS degradation
Water	9	85	80
Acetonitrile	6.2	13	9
Methanol	6.6	7	5
Ethanol	5.2	2	4
Carbon tetrachloride	1.6	0	0
n-Hexane	0.06	0	0

$$TiO_2 + h\nu \rightarrow e^- + h_{vb}{}^+ \tag{1}$$

$$h_{vb}{}^+ \rightarrow h_{tr}{}^+ \tag{1'}$$

$$e^- + O_2 \rightarrow O_2^{\bullet -} \tag{2}$$

$$O_2^{\bullet -} + O_2^{\bullet -} + 2H^+ \rightarrow H_2O_2 + O_2 \tag{3}$$

$$O_2^{\bullet -} + h_{vb}{}^+ \rightarrow O_2 \tag{4}$$

$$O_2^{\bullet -} + h_{tr}{}^+ \rightarrow O_2 \tag{4'}$$

$$OH^- + h_{vb}{}^+ \rightarrow {}^{\bullet}OH \tag{5}$$

$${}^{\bullet}OH + {}^{\bullet}OH \rightarrow H_2O_2 \tag{6}$$

$$e^- + h_{tr}{}^+ \rightarrow \text{recombination} \tag{7}$$

The yields of degradation depend on the solvent polarity; the quickest sulfide degradation is in the aqueous medium and the slowest in *n*-hexane. A possible explanation is that increase of solvent polarity increases active oxygen species on the surface of TiO_2 which raise the percentage of the photodegradation.

3.3. *Effect of photocatalyst amount on the degradation of MPS, MBS, PBS and 3-PBS*

The effect of catalyst TiO_2 amount on photocatalytic degradation of sulfide compounds is presented in Fig. 3. Degradation efficiency of the whole compounds were increased by increasing the photocatalyst amount, then reached the highest value of catalyst amount and finally remain at constant value (i.e. becomes independent of the catalyst concentration). It is interesting to note that this phenomenon has been observed previously in other photocatalytic reaction over TiO_2 [35,36,42,43]. This can be rationalized in terms of availability of active sites on TiO_2 surface and the light penetration of photoactivating light into the suspension. The availability of active sites increases with the suspension of

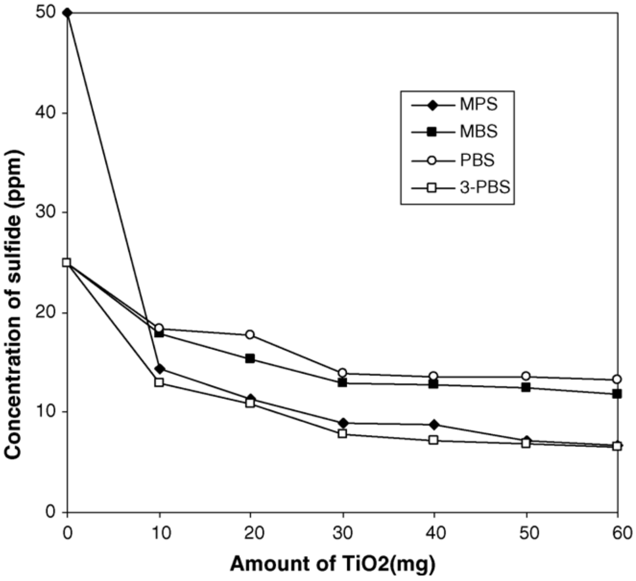


Fig. 3. Sulfide concentration (ppm) vs. amount of TiO_2 (rutile) for runs carried out by using the Pyrex photoreactor ($V = 20$ ml); 400 W high-pressure Hg lamp; flux of $O_2 = 5$ ml/min. (a) MPS; initial pH = 8.0, illumination time 90 s. (b) MBS, (c) PBS, (d) 3-PBS; initial pH = 6, illumination time 3 h.

catalyst loading, but the light penetration and hence the photoactivated volume of the suspension shrinks. Moreover, the decrease in the percentage of degradation at higher catalyst loading may be due to deactivation of activated molecules by collision with ground state molecules. Shielding by TiO_2 may also take place Eq. (8):

$$TiO_2{}^* + TiO_2 \rightarrow TiO_2{}^\# + TiO_2 \tag{8}$$

where $TiO_2{}^*$ is the TiO_2 with active species adsorbed on its surface and $TiO_2{}^\#$ the deactivated form of TiO_2. Agglomeration and sedimentation of the TiO_2 particles were reported. In such condition, part of the catalyst surface probably became unavailable for photon absorption and dye adsorption, thus bringing little stimulation to the catalytic reaction. The crucial concentration depends on the geometry, the working conditions of the photoreactor and the type of UV-lamp (power, wavelength).

The optimum amount of TiO_2 has to be added in order to avoid unnecessary excess catalyst and also to ensure total absorption of light photons for efficient photomineralization. This optimum loading of photocatalyst is found to be dependent on the initial solute concentration. The most effective degradation of the whole sulfide compounds were about 30 mg of TiO_2. As it can be seen from Fig. 3, the initial slopes of linear portion of individual curves are different and this slope decreasing for four sulfide compounds may be due to their physico-chemical properties.

3.4. Effect of illumination time on the degradation of MPS, MBS, PBS and 3-PBS

The reaction profile in Fig. 4 represents the dependence of changes in sulfide compound concentrations on irradiation time in aqueous solutions. The slow kinetic of sulfide compounds degradation after certain time is due to: (a) the difficulty in converting the N- and S-atoms of these compounds into oxidized nitrogen and sulfur compounds respectively, (b) the slow reaction of short chain aliphatics with $^\bullet$OH radicals and (c) the short life-time of photocatalyst because of active sites deactivation by strong by-products deposition (carbon, etc.). Discrepancy between the photocatalytic degradation behaviors of four sulfide compounds may be due to degradation mechanisms and to different products which can be produced during degradation process. As shown in Fig. 4,

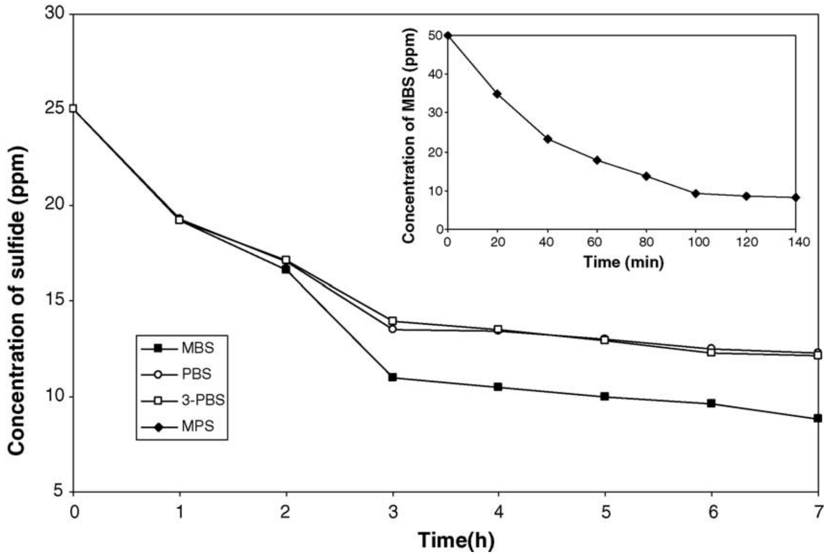


Fig. 4. Organic sulfide concentration (ppm) vs. irradiation time for runs carried out by using the Pyrex photoreactor ($V = 20$ ml); 400 W high-pressure Hg lamp; catalyst amount 30 mg; flux of $O_2 = 5$ ml/min. (a) MPS; initial pH = 8.0, (b) MBS, (c) PBS, (d) 3-PBS; initial pH = 6.

three sulfide compounds MBS, PBS and 3-PBS after 3 h cover the full surface of photocatalyst, whereas the degradation of MPS after 100 min is independent on the UV-light irradiation. It seems that the products of former cases were strongly adsorbed on the TiO_2 surface and blocked it more quickly than the products of MPS degradation. Additional experiments were conducted to verify that the observed mineralization was an intrinsically photocatalytic process as follows: aqueous sample of each organic sulfide was first irradiated with UV-light without adding TiO_2, and in the second experiment, it was stirred with TiO_2 in the absence of UV-light. In both cases, degradation percent was negligible.

3.5. Effect of solution pH on the degradation of MPS, MBS, PBS and 3-PBS

Results of photocatalytic degradation experiments of four sulfide compounds at pH range from 4 to 11 are illustrated in Fig. 5. As seen, the photodegradation percent of three sulfide compounds MBS, PBS and 3-PBS in neutral solution ($pH = 6$) is higher than that of the acidic or basic pH whereas for MPS, the alkaline aqueous solution ($pH = 8–9$) is favorable. It seems that, the pH of solution could affect either the surface properties of the photocatalyst or the chemical form of the substrates, intermediates or products. The interpretation of pH effects on the efficiency of photocatalytic degradation of sulfide compounds is a very difficult task because of its multiple roles. First, it is related to the ionization state of the surface according to the following reactions [44]:

$$TiOH + H^+ \Leftrightarrow TiOH_2{}^+ \quad (9)$$

$$TiOH + OH^- \Leftrightarrow TiO^- + H_2O \quad (10)$$

as well as to that of reactant sulfides and products such as acids and amines. The pH changes can thus influence the adsorption of sulfide molecules onto the TiO_2 surfaces, as an important step for the photocatalytic degradation.

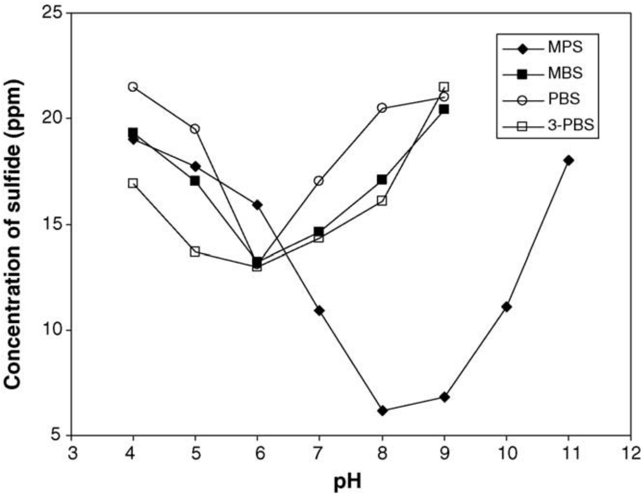


Fig. 5. Organic sulfide concentration (ppm) vs. initial pH for runs carried out by using the Pyrex photoreactor (*V* = 20 ml); 400 W high-pressure Hg lamp; catalyst amount 30 mg; flux of 5 ml/min O_2. (a) MPS; illumination time 90 s, (b) MBS, (c) PBS, (d) 3-PBS; illumination time 3 h.

The point of zero charge (pzc) of the TiO_2 (Degussa P25) is at $pH = 6.8$ [45]. Thus, the TiO_2 surface is positively charged in acidic media ($pH < 6.8$), whereas it is negatively charged under alkaline conditions ($pH > 6.8$). Second, 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 neutral or high pH levels [46–49]. It was stated that in alkaline solution $^\bullet OH$ is easier to be generated by oxidizing more hydroxide ions available on TiO_2 surface, thus the efficiency of the process is logically enhanced. Although it should be noted that in alkaline solution there is a Coulombic repulsion between the negatively charged surface of photocatalyst and the hydroxide anions which could prevent the formation of $^\bullet OH$ and thus decrease the photoxidation [44]. Third, the TiO_2 particles tend to agglomerate under acidic condition and the surface area available for sulfide compounds adsorption and photon absorption would be reduced [18]. An additional explanation for the pH effects can be related to changes in the specification of the sulfide compounds; that is protonation or deprotonation of the sulfides which can change its adsorption characteristics and redox activity.

Three sulfide compounds of MBS, PBS and 3-PBS possess protonation or deprotonation in lower and higher solution pH on the N and NH groups and therefore as we expected via protonation of N atom, they get a positive net charge in lower pH which causes lower photocatalytic degradation yield and in this manner via deprotonation through NH groups they get a negative net charge in higher pH which in turn causes lower photocatalytic degradation yield due to Coulombic repulsion. In consequence, the best solution pH was expected to be neutral pH.

The pH of solution was adjusted using inorganic salts such as: KH_2PO_4, Na_2HPO_4, NaOAc, HOAc, $Na_2B_4O_7$, HCl and NaOH. Anions such as $PO_4{}^{2-}$, $H_2PO_4{}^-$, $B_4O_7{}^{2-}$, Cl^-, and OAc^-, generally decrease the photodegradation rates of sulfides by electrostatic attraction and inhibited the activity of the photocatalyst (TiO_2) by trapping h^+ and $^\bullet OH$ under both acidic and basic conditions [49,50].

3.6. Effect of oxygen on the degradation of MPS, MBS, PBS and 3-PBS

Experiments with a controlled flux of oxygen in aqueous solution were monitored. As the results are presented in Fig. 6, it can be seen that organic sulfides degradation increases in the presence of oxygen with flux of 5 ml/min. Also, no degradation was obtained when titanium dioxide/organic sulfide solutions were sprigged with N_2 instead of O_2 for 20 min before and during UV-light irradiation. In other words, the oxygen is necessary for photocatalytic degradation of these sulfides. It is well known that limitation in photocatalytic degradation efficiency is attributed to the recombina-

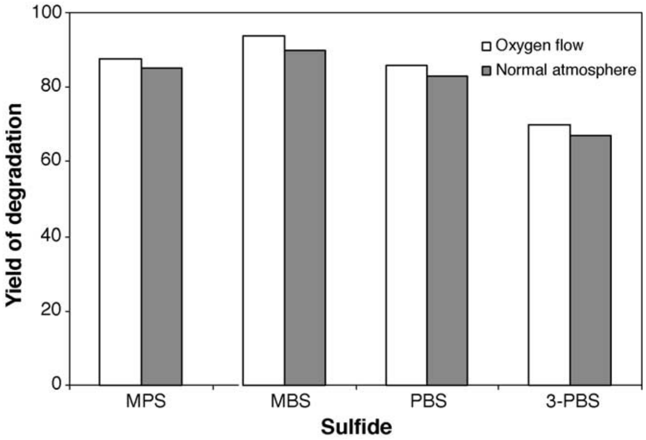


Fig. 6. Photocatalytic degradation percent of MPS and MBS under normal atmosphere and under flux of 5 ml/min O_2: catalyst TiO_2 (rutile), 30 mg; irradiation time 1.5 and 3 h for MPS, MBS, PBS and 3-PBS, respectively.

tion of photogenerated hole–electron pairs. Oxygen adsorbed on the surface of titanium dioxide prevents the recombination process as electrons scavenger. Then the photodegradation reaction efficiency is a function of adsorption sites occupied by oxygen, and oxygen adsorption becomes a limiting factor at very low dissolved oxygen concentration [51].

3.7. Supplementary experiments for support the progression of photocatalytic degradation of MPS, MBS, PBS and 3-PBS

The mineralization of MPS, MBS, PBS and 3-PBS sulfide compounds has been followed using the total organic carbon (TOC) determination in aqueous solution and results are listed in Table 2. It is worth noting that the photocatalytic degradation yields were calculated using both TOC and UV–vis absorbance data. As can be seen from this table, the initial TOC values of MBS, PBS and 3-PBS sulfide compounds are relatively equivalent, as we expected, but of the MPS is higher than the others, which can be related to its higher initial concentration. These results show that total mineralization occur in all cases. Furthermore, calculated photocatalytic degradation yields of sulfide compounds based on absorbance data are in a good agreement with TOC data. For support, the progression of photocatalytic degradation of these sulfides, in each experiment carbon dioxide, ammonia and sulfate ions were detected as mineralization products. Additional experiments were also conducted to verify that the observed mineralization was an intrinsically photocatalytic process as follows: aqueous sample of each organic sulfide was first irradiated with UV-light without adding TiO_2 and in the second experiment it was stirred with TiO_2 in the absence of UV-light. In both cases, the degradation percent was negligible.

Table 2
Calculation of photocatalytic degradation yield of sulfide compounds based on TOC and absorbance data

Sulfide	Initial TOC	Final TOC	Yield of degradation based on TOC[a]	Yield of degradation based on Abs[b]
MPS	33.9	4.5	85	87
MBS	14.6	3.5	73	79
PBS	17	2	66	68
3-PBS	16	0.3	95	98

[a] Calculation based on TOC data.
[b] Calculation based on absorbance data.

4. Conclusion

The present work has shown that the mentioned organic sulfides can be degraded using a photocatalytic process. The obtained results have specified the effect of some operational parameters on the process efficiency leading to the degradation of organic sulfides. Mineralization of organic sulfides using photocatalytic method showed high efficiency. The photocatalytic activity of TiO_2 (rutile) was much better than ZnO or TiO_2 (anatase). The effect of catalyst loading on photodegradation of organic sulfides was determined. The degradation efficiency increased with primary increase in catalyst amount up to 30 mg TiO_2 (rutile) as the optimum loading, but further increase has no significant improvement. Results obtained for different pH, showed that the process will proceed in natural solution much better than in acidic or basic medium. In summary, the proposed heterogeneous photocatalytic degradation of organic sulfides which are important industrial wastewater pollutants, can be applied as practical methods for environmental decontamination.

Acknowledgment

The authors wish to thank the University of Isfahan for financially supporting this work.

References

[1] V. Iliev, A. Ileva, L. Bilyarska, J. Mol. Catal. A: Chem. 126 (1997) 99–108.
[2] J.R. Salazar, in: R.A. Mayers (Ed.), Handbook of Petroleum Processes, Part 9, McGraw-Hill, New York, 1986.
[3] A.V. Vorontsov, E.V. Savinov, C. Lion, P.G. Smironiotis, Appl. Catal. B: Environ. 44 (2003) 25–40.
[4] C. Wilson, D.M. Hirst, Prog. React. Kinet. 21 (1996) 69–75.
[5] A.V. Vorontsov, E.V. Savinov, L. Davydov, P.G. Smironiotis, Appl. Catal. B: Environ. 32 (2001) 11–24.
[6] Y. Takahara, K. Kato, R. Inaba, H. Iwata, Jpn. J. Public Health 40 (1993) 29.
[7] H. Nishikawa, Y. Takahara, J. Mol. Catal. A: Chem. 172 (2001) 247–251.
[8] H.M. Freeman, Incinerating Hazardous Wastes, Technomiv Publishing Co., Lancaster, PA, 1988, p. 375.
[9] B. Mills, Filtr. Separat. 32 (1995) 147–152.
[10] Y.-C. Yang, F.J. Berg, L.L. Szafraniec, W.T. Beavdry, C.A. Bunton, A. Kumar, J. Chem. Soc., Perkin Trans. 2 (1997) 607–613.

[11] Y.-C. Yang, J.A. Baker, J. Richardward, Chem. Rev. 92 (1992) 1729–1743.

[12] S. Franke, P. Franz, W. Warnke, Lehrbuch der Militarchemie, Deutscher Militarverlag, Berlin, 1976.

[13] D.V. Kozlov, A.V. Voronstov, P.G. Smirniotis, E.N. Sarinov, Appl. Catal. B: Environ. 42 (2003) 77–87.

[14] M.R. Hoffman, S.T. Martin, W. Choi, D.W. Bahnemann, Chem. Rev. 95 (1995) 69–96.

[15] A. Fujishima, T.N. Rao, D.A. Tryk, J. Photochem. Photobiol. C: Photochem. Rev. 1 (2000) 1–21.

[16] A. Mills, S.L. Hunte, J. Photochem. Photobiol. A: Chem. 108 (1997) 1–35.

[17] D.F. Ollis, H. Al-Ekabi (Eds.), Photocatalytic Purification and Treatment of Water and Air, Elsevier, London, UK, 1993.

[18] M.A. Fox, M.T. Dulay, Chem. Rev. 93 (1993) 341–357.

[19] S. Hager, R. Bauer, G. Kudielka, Chemosphere 11 (2000) 1219–1225.

[20] P.V. Kamta, J. Phys. Chem. B 106 (2002) 7729–7744.

[21] R. Nakamura, A. Imanishi, K. Murakoshi, Y. Nakato, J. Am. Chem. Soc. 125 (2003) 7443–7450.

[22] S. Sato, K. Ueda, Y. Kawasaki, R. Nakamura, J. Phys. Chem. B 106 (2002) 9054–9058.

[23] R.B. Draper, M.A. Fox, Langmuir 6 (1990) 1396–1402.

[24] A.Y. Nosaka, T. Fujiwara, H. Yagi, H. Akutsu, Y. Nosaka, Langmuir 19 (2003) 1935–1937.

[25] M.A. Fox, M.T. Dulay, J. Photochem. Photobiol. A: Chem. 98 (1996) 91–101.

[26] D.P. Colombo Jr., R.M. Bowman, J. Phys. Chem. 100 (1996) 18445–18449.

[27] A. Furube, T. Asahi, H. Masuhara, M. Anpo, Res. Chem. Intermed. 27 (2001) 177–187.

[28] T. Tachikawa, S. Tojo, M. Fujitsuka, T. Majima, Chem. Phys. Lett. 382 (2003) 618–625.

[29] R.F. Howe, M. Graetzel, J. Phys. Chem. 91 (1987) 3906–3909.

[30] D.C. Hurum, A.G. Agrios, K.A. Gray, T. Rajh, M.C. Thurnauer, J. Phys. Chem. B 107 (2003) 4545–4549.

[31] Y. Nosaka, M. Kishimoto, J. Nishino, J. Phys. Chem. B 102 (1998) 10279–10283.

[32] Y. Mao, C. Schoeneich, K.-D. Asumus, J. Phys. Chem. 95 (1991) 10080–10089.

[33] Y. Nakaoka, Y. Nosaka, J. Photochem. Photobiol. A: Chem. 110 (1997) 299–305.

[34] M.H. Habibi, S. Tangestaninejad, B. Yadollahi, Appl. Catal. B: Environ. 33 (2001) 57–63.

[35] M.H. Habibi, S. Tangestaninejad, B. Yadollahi, J. Ind. Pollut. Contr. 24 (2000) 80–89.

[36] M.H. Habibi, M. Khaledisardashti, M. Montazerozohori, Annal di Chim. 94 (2004) 421–428.

[37] A.I. Vogel, A.R. Tatchell, B.S. Furnis, A.J. Hannaford, P.W.G. Smith, Vogel’s Textbook of Practical Organic Chemistry, 5th ed., Wiley, New York, 1989, p. 789.

[38] L. Gilbert, Mercier, in: M. Guisent, J. Barbier, J. Barrault, C. Bouchoule, D. Duprez, G. Perot, C. Mintassier (Eds.), Heterogeneous Catalysis and Fine Chemicals III, Elsevier, The Netherlands, 1993, p. 51.

[39] S. Sakthivela, B. Neppolianb, M.V. Shankarb, B. Arabindoob, M. Palanichamyb, V. Murugesanb, Sol. Energy Mater. Sol. Cell. 77 (2003) 65–82.

[40] T. Ohno, K. Sarukawa, M. Matsumura, J. Phys. Chem. B 105 (2001) 2417–2420.

[41] T. Hirakawa, Y. Nosaka, Langmuir 18 (2002) 3248–3254.

[42] R.L. Davis, J.L. Gainer, G. O’Neal, I.W. Wu, Water Environ. Res. 66 (1994) 50–53.

[43] Z. Mengyne, C. Shifn, T. Yaown, J. Chem. Technol. Biotechnol. 64 (1995) 339–344.

[44] I.K. Konstantinou, T.A. Albanis, Appl. Catal. B: Environ. 49 (2004) 1–14.

[45] I. Poulios, I. Tsachpinis, J. Chem. Technol. Biotechnol. 74 (1999) 349–357.

[46] W.Z. Tang, C.P. Huang, Water Res. 29 (1995) 745–756.

[47] S. Tunesi, M. Anderson, J. Phys. Chem. 95 (1991) 3399–3405.

[48] C. Korman, D.W. Bahnemann, M.R. Hoffman, Environ. Sci. Technol. 25 (1991) 494–500.

[49] C. Hu, Yu Jimmy C, Z. Hao, P.K. Wong, Appl. Catal. B: Environ. 46 (2003) 35–47.

[50] K. Wang, J. Zhang, L. Lou, S. Yang, Y. Chen, J. Photochem. Photobiol. A: Chem. 165 (2004) 201–207.

[51] E. Pelizzetti, Sol. Energy Mater. Sol. Cell. 38 (1995) 453–457.