Photocatalytic degradation of dibenzothiophene using La/PEG-modified TiO_2 under visible light irradiation

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Abstract While the photocatalytic degradation of various organic compounds under UV light irradiation has been widely investigated, visible-light-induced photocatalytic degradation of low levels of pollutants such as dibenzothiophene (DBT) is occasionally reported. In the present work, lanthanide/polyethylene glycol-modified TiO₂ (La/PEG/TiO₂) has been successfully synthesized by a sol–gel method. The photocatalyst was characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscopy, UV–Vis diffusive reflectance spectroscopy, and energy dispersive X-ray analysis. Moreover, the photocatalytic degradation of DBT under visible light irradiation is investigated for the first time using the newly synthesized photocatalyst. The effects of important operational parameters such as initial DBT concentration, catalyst loading, pH, and amount of H₂O₂ on the degradation efficiency were studied. Kinetics parameters of the photocatalytic oxidation of DBT were also calculated. The results show that DBT decomposition occurs according to the Langmuir–Hinshelwood mechanism. The degradation products were analyzed by the GC–MS technique.

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Introduction

Dibenzothiophene (DBT) is a heterocyclic molecule containing sulfur present in petroleum, and its degradation has been studied as the model organic sulfur compound in crude oil [1]. The presence of sulfur in petroleum products is considered as one of the most important sources of environmental contamination, since it leads to the release of sulfur dioxide (SO₂), as a major air pollutant responsible for acid rain, upon combustion [2]. Hence, the level of sulfur in such compounds is continuously being reduced by regulations to the lowest levels ever. For instance, the Environmental Protection Agency has issued a series of tenacious regulations in order to decrease sulfur content in diesel fuel to <15 ppm in 2013 [3].

The widely used technology to remove sulfur content from liquid petroleum streams is the conventional hydrodesulfurization (HDS) method [4, 5]. Although HDS is highly efficient in removing thiols, sulfides, and disulfides, it has several inherent disadvantages such as heavy cost in operating and capital, energy-intensiveness, and its ineffectiveness in removing sulfur-containing compounds such as DBT [6, 7]. Therefore, new approaches have attracted attention for being more efficient alternatives.

Oxidative desulfurization (ODS) is one of the promising new methods being investigated as an alternative technology for the deep desulfurization of fuel oils. In comparison with conventional HDS, ODS has attractive features such as high efficiency, lower cost of operation, and mild temperature and pressure conditions [8-10]. In particular, photocatalytic ODS is of great interest. In this process, free radicals are formed via irradiation by some kind of energy source in the presence of a photocatalyst in order to photo-oxidize sulfur compounds to CO_2 , SO_4^{2-} , sulfoxides, and sulfones [11-13]. TiO₂ has been widely used as a photocatalyst because of its merits which include optical and electronic properties, high level of photocatalytic activity, low cost, chemical stability, and non-toxicity [14-18]. For instance, to improve sulfur removal, TiO_2 has been investigated for the oxidation of DBT [19–21]. Matsuzawa et al. [19] studied the effect of adding H₂O₂ and ultrasound irradiation to the TiO₂-containing system for the photooxidation of DBT. They compared four kinds of TiO₂ powder as photocatalysts and found that P25 showed the highest photooxidation rate. However, the conversion of DBT was <40 % after irradiation for 10 h. Robertson and Bandosz [20] evaluated a new titanium(IV) oxide-hectorite nanofilm photocatalyst in the photo-oxidation of DBT in tetradecane, as a model for diesel fuel. They made a comparison with a commercially available TiO₂ catalyst, Degussa P25. Their results indicated that the outlined process was effective in reducing sulfur levels to below 10 ppm. Zhang and coauthors [21] investigated photocatalytic oxidation of DBT using titanium silicalite zeolite as photocatalyst with hydrogen peroxide at ultraviolet lamp irradiation. They found that DBT was photooxidized successfully. In all the mentioned works, the degradation of DBT was performed under UV light,

while, to our knowledge, there is no publication on the photocatalytic degradation of DBT under visible light irradiation.

Although TiO₂ is now the most widely researched photocatalyst for various applications, it is restricted to UV light due to its wide band gap energy of ~ 3.2 eV [14, 22]. Therefore, the development of a TiO₂ photocatalyst that shows a high level of activity under visible light with a view towards industrial applications is needed. Notably, in order to extend its light absorption into the visible region, several attempts have been made to lower the band gap energy by doping TiO₂ with transition metals/non-metal elements or other semiconductors, dyes, and metal and carbon nanoparticles [23-27]. For example, N, S, or C anion-doped TiO₂ photocatalysts have been reported, having an anatase form that shows a relatively high level of activity when irradiated by visible light [28–30]. In addition, Adams et al. [31] reported that the use of lanthanide doping in a titania sol-gel enhances the electron hole separation and also widens the absorption potential into the visible region. Furthermore, as a strategy to achieve a more efficient photocatalyst, polyethylene glycol (PEG) was added to the photocatalyst during the synthesis process. It increases not only the specific surface areas but also the visible light adsorption of the synthesized photocatalyst [32-34].

In the present work, lanthanide/PEG-modified TiO₂ (La/PEG/TiO₂) has been synthesized for the first time using a sol–gel method. Its application has been evaluated through the photocatalytic degradation of DBT in acetonitrile under visible light. Moreover, the effects of important operational parameters such as initial DBT concentration, catalyst loading, pH, and the amount of H_2O_2 on the degradation efficiency were studied. Kinetics parameters of the photocatalytic oxidation of DBT were also calculated.

Experimental

Chemicals

All reagents and solvents used in experiments are available commercially and were used without further purification. DBT (>98 %) was purchased from Fluka (Buch, Switzerland). Acetic acid, acetonitrile, titanium(IV) isopropoxide (TTIP), lanthanum(III) nitrate hexahydrate and PEG (MW = 4,000) were obtained from Merck. The following equipment was used: a 400 W xenon lamp to produce visible light at 420 nm, an ultraviolet cutoff filter (Kenko,) to allow the passage of light with wavelengths longer than 400 nm in order to ensure that the irradiation occurred under visible light only, a glass vessel, X-ray diffraction (XRD) patterns (Philips X'pert Pro MPD model) with Cu K α radiation (40 kV, 40 mA) at 20 angles from 10° to 80° and with a scan speed of 4 min⁻¹, field emission scanning electron microscope Hitachi S4160, TEM Hitachi Model H-9000NAR instrument with accelerating voltage of 200 kV, UV–Vis spectrometer (Ava Spec-2048TEC spectrometer from 350 to 750 nm wavelengths), a zeta meter (Zeta Meter, USA) and an Agilent 7890A GC coupled with an Agilent 5975C MSD (Agilent Technologies, Santa Clara, CA, USA).

Catalyst preparation

The catalyst was prepared by a sol–gel process as follows: TTIP was dissolved and hydrolyzed in glacial acetic acid at a mole ratio of 1:10 at 0 °C. The solution was stirred magnetically for 30 min (mixture A). La(NO₃)₃·6H₂O (La:Ti mol ratio = 0.3 %) and PEG (PEG: Ti = 0.5 molar ratio) were dissolved in appropriate amount of deionized water (mixture B). Mixture A was then added dropwise into mixture B for 70 min under vigorous stirring. The resulting solution was ultrasonicated for 20 min at 0 °C and stirred continuously for 260 min. Subsequently, the solution was again ultrasonicated and held for a day at room temperature in the dark. The solution was then gelated at 76 °C and dried at 120 °C. The dried photocatalyst was ground with a mortar and pestle into fine powders, and finally calcined at 550 °C for 3 h to prepare the required nanoparticle photocatalysts. Bare TiO₂ was synthesized similar to Philips X'pert Pro MPD model) with Cu K radiation above method, without use of La(NO₃)₃·6H₂O and PEG in mixture B.

Photocatalytic test

Photo-oxidation trials were performed in a quartz tube reactor using the 400 W xenon lamp which produces light spectra similar to that of solar radiation. Photocatalytic tests were carried out by stirring at room temperature an acetonitrile solution of the sulphur compound (25–500 ppm) in the presence of photocatalyst (from 10 to 150 mg). Some experiments were carried out by adding the required amount of H_2O_2 to obtain an initial 10^{-3} M concentration of H_2O_2 before starting the irradiations. Photocatalytic experiments comprised two phases: an equilibration phase and a reaction phase. In the first phase (equilibration), the reaction suspension was stirred continuously in the dark for 20 min to ensure adsorption/desorption equilibrium. For the second phase, the solution was irradiated for 5 h and samples (5 ml) were collected from the glass vessel and analyzed to determine substrate concentration and reaction products. Prior to analysis, samples were centrifuged to remove fine photocatalyst particles. A gas chromatograph (GC-7890A; Agilent) equipped with the mass spectrometer (MS-5975C; Agilent) was mainly used for the analysis.

Results and discussion

Characterization of synthesized photocatalyst

XRD patterns analysis

Figure 1 shows the XRD patterns of TiO₂ and La/PEG/TiO₂. The diffraction patterns of TiO₂ and the sol–gel-prepared catalyst only show anatase as the crystalline phase. Therefore, the broader peak width and slight shift to a higher angle was observed for the La/PEG/TiO₂ sample. Evidently, the dominant peaks of anatase at 25.2° and 25.48° for TiO₂ and La/PEG/TiO₂, respectively, may indicate slight lattice shrinkage of some of the TiO₂ lattices caused by substitution of the dopants. Furthermore, the



Fig. 1 XRD patterns of the La/PEG/TiO₂ and pure TiO₂

broader XRD peak width possibly implied that the crystallites of the doping sample were smaller relative to pure TiO₂. Therefore, based on these results, the average crystalline particle size of TiO₂ was calculated by the Scherrer equation from the broadening of the anatase peaks. The La/PEG/TiO₂ sample revealed unique small crystallite sizes (23 nm) compared to TiO₂ (36 nm) suggesting that the presence of La and PEG retarded the growth of the TiO₂ crystalline phase.

Scanning electron microscope (SEM) analysis

The typical SEM image of La/PEG/TiO₂ is shown in Fig. 2. It can be clearly seen that the catalyst is composed of nanoparticles.

As can be seen, the surface of La/PEG/TiO₂ cannot be described as a homogeneous layer of material (Fig. 2). Rather, it is made up of agglomerations of nanoscale particles of hectorite (outer layer), stuck together into features, which in some cases are nearly a micrometer across. The individual crystals appear to span a range of about 15–25 nm.

Transmission electron microscopy (TEM) analysis

Figure 3 is the TEM image of La/PEG/TiO₂. As shown in Fig. 3, the synthesized photocatalyst had a mesoporous structure and the average particle size of the La/ PEG/TiO_2 was about 20 nm.

UV-Vis diffuse reflectance spectra

The optical absorption properties that are relevant to the electronic structure feature of the photocatalytic materials are recognized as the key factors in determining their



Fig. 2 SEM image of La/PEG/TiO₂ catalyst



Fig. 3 TEM image of La/PEG/TiO₂ catalyst

photocatalytic activity. Here, the optical absorption properties of the as-prepared La/ PEG/TiO₂ were investigated by UV–Vis/DRS; for comparison, the La-doped TiO₂ as well as pure TiO₂ were also tested (Fig. 4). The band gap energies (E_g) of La/PEG/TiO₂ and La-doped TiO₂ can be estimated from the wavelength values corresponding to the intersection point of the vertical and horizontal parts of the spectra using the following equation [35, 36]:

$$E_{\rm g}=\frac{hc}{\lambda},$$

where E_g is the band gap energy (eV), *h* is the Planck's constant, *c* is the light velocity (m/s) and λ is the wavelength (nm). The band gap energies of La/PEG/TiO₂ and La-doped TiO₂ were calculated, and are 2.45 and 2.55 eV, respectively.

The red shift of the absorption edge and the lower band gap of La/PEG/TiO₂ is probably due to the lower band gap (E_g) of La/PEG/TiO₂ in comparison to that of La-doped TiO₂. It is known that a red shift of the absorption edge would mean a reduction in band gap energy and an enhancement of photocatalytic efficiency. In other words, with lower band gap energy in comparison to that of La-doped TiO₂, La/PEG/TiO₂ can be excited to produce more electron–hole pairs under visible light, which could lead to higher photocatalytic activity. Furthermore, the addition of PEG introduces some extra trap states (impurity levels) within the valence and conduction bands of TiO₂ [37]. The results indicate that the whole La/PEG/TiO₂ sample had a better optical absorption in the region of 300–700 nm owing to the presence of both La and PEG compared with the La-doped TiO₂ and the pure TiO₂. The enhancement of absorbance in the UV–Vis region increases the number of photogenerated electrons and holes to participate in the photocatalytic reaction, which can enhance the photocatalytic activity of TiO₂ [38].



Fig. 4 The UV–Vis diffuse reflectance spectra of pure TiO₂, La-doped TiO₂, and La/PEG/TiO₂

Energy dispersive X-ray (EDX) analysis

Energy dispersive X-ray spectroscopy (EDX) is an analytical technique for element analysis, and the chemical characterization of the La/PEG/TiO₂ has been obtained. EDX analysis of the La/PEG/TiO₂ is illustrated in Fig. 5. This figure shows the presence of Ti, La, and O elements on the as-prepared photocatalyst. The Ti and O peaks result from the TiO₂ particles; the La element indicates the presence of lanthanide in the La/PEG/TiO₂ photocatalyst.

Effect of initial DBT concentration

The effect of the presence of La/PEG/TiO₂ on the photooxidation of DBT in acetonitrile was assessed from plots of $-\ln (C_t/C_0)$ versus *t* obtained with and without the photocatalyst (Fig. 6). It is important to analyze the effect of different DBT concentrations because DBT concentration varies in different crude oil streams. In our study, the different DBT concentrations ranged from 25 to 500 mg L⁻¹. The results showed that the degradation efficiency decreased with the increased concentration of DBT (Fig. 6). When the concentration of DBT increases, the photons can be interrupted before they can reach the photocatalyst surface; hence, the absorption of photons by the photocatalyst decreases, and, consequently, the degradation efficiency decreases. It is suggested that the optimal initial DBT concentration for the photocatalytic degradation in the experiment is 250 mg L⁻¹, and the photocatalytic degradation reached 67.24 % in this condition.



Fig. 5 EDX spectrum of La/PEG/TiO₂ catalyst



Fig. 6 Effect of initial DBT concentration on photocatalytic oxidation, [La/PEG/TiO₂]: 0.5 g L^{-1} , pH 7.00

Effect of photocatalyst concentration

The influence of the photocatalyst concentration on the degradation of DBT has been investigated using different concentrations of La/PEG/TiO₂ varying from 0.1 to 1.5 g L⁻¹ for DBT (Fig. 7). The initial concentration of DBT and irradiation conditions are identical on all the runs. In the absence of the catalyst, almost no oxidization of DBT was observed. However, it can be seen that the addition of the photocatalyst promotes the oxidation of DBT, since the rate of OH[•] formation and charge transfer can be accelerated by the addition of the photocatalyst.

A photocatalyst concentration of 0.5 g L^{-1} appears to be the best condition considering the degradation of DBT, whereas, in the presence of lower photocatalyst loading smaller and in the case of higher loading, almost identical photonic efficiencies were observed. The reason for this is that, at a certain photon flux impinging on the suspension, the number of photons absorbed increases with the amount of photocatalyst up to a point when the presence of additional amounts of photocatalyst do not lead to further photon absorption.

pH effect

The pH of the aqueous solution is one of the important environmental parameters, significantly influencing the physicochemical properties of semiconductors, including the charge on the photocatalyst particle, the aggregation numbers of particles, and the positions of the conductance and valence bands [39].

The effect of initial pH on the photocatalytic degradation of DBT was studied. In the alkaline range, the pH was varied using aqueous NaOH, whereas in the acidic



Fig. 7 Effect of photocatalyst concentration on photocatalytic oxidation of DBT in acetonitrile, $[DBT]_0$: 250 mg L⁻¹, pH 7.00

range, the pH was varied using HClO₄. An initial DBT concentration of 250 mg L^{-1} and catalyst loading of 0.5 g L^{-1} were used in all these experiments. The experimental results are shown in Fig. 8.

As observed in Fig. 8, no significant differences were found in the DBT removal within the tested reaction period of 5 h with different pH of the initial solution. However, the acidic pH showed a better performance than that of neutral or alkaline pH. To investigate the surface charge of La-doped TiO₂, and La/PEG/TiO₂, the zeta potentials (ζ) of the photocatalysts were measured on a zeta meter. A ζ value of -40.3 ± 4.12 mV was measured for pure undoped TiO₂. Upon doping with La, the ζ value of La-doped TiO₂ decreased to about -27.3 ± 2.95 mV, and this value was further decreased to -22.8 ± 4.06 mV upon addition of PEG to the photocatalyst structure. Possible explanations for the above results are: at acidic pH, the HO_2^{\bullet} radical is also able to form, and this can compensate for the decrease in the generated OH[•] radicals. At theeutral and alkaline pH, the results indicated that the as-prepared photocatalyst possessed surface negative charges, resulting in negative ζ values. Moreover, the DBT anions have been studied [40]. Therefore, there is a Coulombic repulsion between the surface of La/PEG/TiO2 and DBT anion at the neutral and alkaline pH. The Coulombic repulsion can limit the adsorption of the DBT anion on the surface of La/PEG/TiO2 and the diffusion of OH[•] radicals toward the DBT anions for the subsequent reaction. Therefore, the photocatalytic degradation rate would be unavoidably decreased in neutral or alkali solutions.

Effect of addition of hydrogen peroxide (H_2O_2)

The effect of the oxidant amount on the desulfurization rate were investigated experimentally. The experimental results are shown in Fig. 9. According to Fig. 9,



Fig. 8 Effect of pH on photocatalytic oxidation of DBT in acetonitrile, $[La/PEG/TiO_2]$: 0.5 g L⁻¹, $[DBT]_0$: 250 mg L⁻¹

when the oxidant amount rose from 1 to 3 mL, a steady increase in the desulfurization rate of DBT was observed, and the value of the desulfurization rate reached the maximum at 3 mL. When the oxidant amount was further increased, the desulfurization rate decreased.

It is clear that the addition of hydrogen peroxide in this process has two competing effects: (1) increasing the concentration of hydroxyl radicals in the reaction media; and (2) decreasing the average light intensity within the solution due to the absorption of visible light by H_2O_2 . The proper H_2O_2 concentration has been found to enhance the degradation rate of DBT due to the more efficient generation of hydroxyl radicals (OH[•]) and the inhibition of the recombination of electron/hole (e^{-}/h^{+}) pairs according to the following equation [41]:

$$e^- + H_2 O_2 \to OH^- + OH^{\bullet}. \tag{1}$$

When excessive H_2O_2 is present, it is possible that H_2O_2 scavenges reactive oxidative species like OH[•] radicals (Eq. 2), and inhibits the subsequent degradation reactions [42].

$$H_2O_2 + OH^{\bullet} \to H_2O + HO_2^{\bullet}.$$
 (2)

Although confirmative evidence is needed, the competition for OH^{\bullet} and the formation of less reactive HO_2^{\bullet} may explain the reduced reaction rate at a higher concentration of H_2O_2 shown in Fig. 9.

In addition, in order to exhibit the role of La and PEG in the improvement of photocatalytic activity of La/PEG/TiO₂ under visible light irradiation, at and undoped TiO₂ loading of 0.5 g L⁻¹, and with the oxidant amount of 3 mL on the condition of visible light irradiations, the effects of the presence of only H_2O_2 , H_2O_2



Fig. 9 Effect of addition of hydrogen peroxide on photooxidation of DBT in acetonitrile, [La/PEG/ TiO_2]: 0.5 g L⁻¹, pH 7.00, [DBT]₀: 250 mg L⁻¹

and undoped TiO_2 on the desulfurization efficiency were investigated experimentally. The experimental results are shown in Fig. 10.

As can be seen from Figs. 9 and 10, the DBT desulfurization efficiency in the presence of only H_2O_2 and undoped TiO₂ are slower than the photo-oxidation of DBT when La/PEG/TiO₂ was used. Therefore, the increase in the photooxidation of DBT for the La/PEG/TiO₂–H₂O₂ system may be attributed to direct oxidation by H_2O_2 as well as the role of La and PEG in the improvement of photocatalytic activity of La/PEG/TiO₂ under visible light irradiation.

Kinetics of photocatalytic oxidation of DBT

Kinetics studies on the photocatalytic rate of the contaminants are useful for process scale-up. In general, the reaction kinetics follows the Langmuir–Hinshelwood mechanism given in the following equation [43]:

$$r_0 = -\frac{\mathrm{d}C}{\mathrm{d}t} = \frac{kKC}{1+KC}.\tag{3}$$

where r_0 is the reaction rate (mg L⁻¹ min⁻¹), C is the concentration of reactant in solvent (mg L⁻¹), k is the limiting degradation rate constant at maximum coverage of the adsorbed pollutant (mg L⁻¹ min⁻¹), K is the Langmuir adsorption constant of pollutants that adhere to the photocatalyst surface (L mg⁻¹), and t is the illumination time (min). This model assumes adsorption of reactants, surface reaction, and desorption of products; where the reaction is the rate limiting step. The expression can be rewritten and integrated to:



Fig. 10 The effects of the presence of only H_2O_2 , H_2O_2 and undoped TiO₂ on the desulfurization efficiency of DBT in acetonitrile, pH 7.00, [DBT]₀: 250 mg L⁻¹

$$\frac{\ln\left(\frac{C_0}{C}\right)}{(C_0 - C)} = \frac{k \cdot K}{(C_0 - C)}t - K,\tag{4}$$

where C_0 is the initial concentration. It has been suggested that, at very dilute concentrations ($C_0 < 10^{-3} \text{ mol } \text{L}^{-1}$), *KC* becomes $\ll 1$, and the reaction is of apparent first-order [44] and the equation is simplified to:

$$\ln\left(\frac{C_0}{C}\right) = k \cdot Kt = k't,\tag{5}$$

where k' represents the pseudo-first-order rate constant. A plot of the logarithm of the relative concentration of the pollutant $\left(\ln\left(\frac{C_0}{C}\right)\right)$ as a function of illumination time yields a straight line with the slope corresponding to the first-order constant (Fig. 6). From the data obtained during this study, the values of k' for different initial concentrations of DBT are given in Table 1 and the k, K, and $k \cdot K$ for various C_{DBT} are listed in Table 2.

According to Table 1, it is clear that the reported rate constants are not pseudofirst-order rate constants at all since they change with the initial concentration of

DBT. In Table 2, the k, K, and $k \cdot K$ obtained from plots of $\frac{\ln{\binom{C_0}{C}}}{(C_0 - C)}$ versus $\frac{t}{(C_0 - C)}$ are shown. As can be seen from the table, the $k \cdot K$ values are of the same order of magnitude, but not equal, to the k' values reported in Table 1. It could also be

Table 1 Apparent pseudo-first- order rate constants for DBT	$C_0 \;(\mathrm{mg}\;\mathrm{L}^{-1})$	$k' \times 10 \;(\min^{-1})$	R^2
degradation in acetonitrile	25	3.25	0.988
	100	1.64	0.981
	250	1.26	0.973
	500	0.78	0.982
	-		

Table 2 DBT Langmuir– Hinshelwood parameters at the studied initial concentration values	$\frac{C_0}{(\text{mg L}^{-1})}$	$k \pmod{(\text{mg } \text{L}^{-1} \text{min}^{-1})}$	$\frac{K \times 10}{(\text{L mg}^{-1})}$	$k \cdot K \times 10$ (min ⁻¹)	R^2
	25	2.36	1.35	3.18	0.983
	100	2.41	0.98	2.36	0.987
	250	2.65	0.68	1.80	0.954
	500	2.47	0.61	1.51	0.961
Table 3 Comparison betweenthe rate constants obtained formineralization and degradationof DBT at pH 3, 7, and 10	рН	pH k' × 10 (min mineralizatio		$k' \times 10 \text{ (min}^{-1})$ h degradation	
	3.00	3.00 1.12		4.43	
	7.00	0.94		3.18	
	10.00	0.51		1.58	

proved that the decrease in the k' values with increasing C_0 is due to the light as limiting reagent. From these tables it can be concluded that, in fact, for photocatalytic degradation of DBT in acetonitrile the Langmuir–Hinshelwood mechanism is operating since the experimental points can be fit to Eq. (3).

Products formed by photocatalytic oxidation of DBT

An attempt was made to identify the photo-oxidation products formed in the photocatalytic degradation of DBT in acetonitrile through GC–MS analysis. The main products identified by GC–MS were DBT 5-oxide (DBT sulfoxide) and DBT 5,5-dioxide (DBT sulfone). The products were identified based on their molecular ion and mass spectrometric fragmentation peaks. The similarities of the main products compared with GC–MS NIST library ranged from 88 to 95 %. The formation of these products is consistent with the results obtained by Matsuzawa et al. [19].

DBT mineralization

DBT mineralization during the photocatalytic oxidation was followed by measuring the COD (chemical oxygen demand) at pH 3, 7, and 10. An initial DBT concentration of 25 mg L⁻¹ and catalyst loading of 0.5 g L⁻¹ were used in all these experiments. In a typical sample, reaction aliquots (3 mL) were taken at different reaction times and the COD in each aliquot was determined using a colorimetric method [45], in which the total organic sample content was oxidized in a closed system using sulfuric acid and potassium dichromate for 2 h at 150 °C. The solution absorbance at 600 nm was measured [12]. From this absorbance, the solution COD was obtained using a calibration curve made with potassium hydrogen phthalate. The apparent pseudofirst-order rate constants for DBT mineralization are obtained from the slope of plots of ln COD versus time. These rate constants are shown in Table 3 where they are compared with the corresponding rate constants for DBT degradation. As shown in Table 3, the rate constants for mineralization (following COD) are 75, 70, and 67 % slower than the DBT degradation at pH 3, 7, and 10, respectively. The mineralization rate far below the degradation rate indicates the formation of some stable organic intermediates during the photocatalytic process.

Conclusion

La/PEG/TiO₂ was successfully synthesized using a sol–gel method. The addition of lanthanide and PEG to the photocatalyst structure improved the photocatalysis of TiO₂ under visible light irradiation. This new photocatalysis was used for the degradation of DBT under visible light. The results of this study clearly demonstrate the importance of choosing the optimum degradation parameters (DBT concentration, pH, catalyst concentration, etc.) to obtain a high degradation rate of the model pollutant. The optimal values of the operation parameters under the related constraint conditions were found at initial DBT concentration of 250 mg L⁻¹, H₂O₂ amount 3 mL, initial pH of 3, and catalyst loading 0.5 g L⁻¹. Moreover, DBT decomposition occurs according to the Langmuir–Hinshelwood mechanism.

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References

- 1. D.J. Monticello, Biodesulfurization and the upgrading of petroleum distillates. Curr. Opin. Biotechnol. 11(6), 540-546 (2000)
- U.S. Environmental Protection Agency, Fuel sulfur effects on exhaust emissions. http://www.epa. gov/otaq/models/mobile6/m6tech.htm. Accessed May 2013
- U.S. Environmental Protection Agency, from CoAP, New motor vehicles, and H-DEaVS, Requirements HDFSC. http://www.epa.gov/fedrgstr/EPA-AIR/2001/January/Day-18/a01a.htm. Accessed May 2013
- F.G. Petzold, J. Jasinski, E.L. Clark, J.H. Kim, J. Absher, H. Toufar, M.K. Sunkara, Nickel supported on zinc oxide nanowires as advanced hydrodesulfurization catalysts. Catal. Today 198(1), 219–227 (2012). doi:10.1016/j.cattod.2012.05.030
- L. Wang, B. Sun, F.H. Yang, R.T. Yang, Effects of aromatics on desulfurization of liquid fuel by πcomplexation and carbon adsorbents. Chem. Eng. Sci. 73, 208–217 (2012). doi:10.1016/j.ces.2012. 01.056
- J. Zhang, W. Zhu, H. Li, W. Jiang, Y. Jiang, W. Huang, Y. Yan, Deep oxidative desulfurization of fuels by Fenton-like reagent in ionic liquids. Green Chem. 11(11), 1801–1807 (2009). doi:10.1039/ B914130H
- M.C. Capel-Sanchez, J.M. Campos-Martin, J.L.G. Fierro, Removal of refractory organosulfur compounds via oxidation with hydrogen peroxide on amorphous Ti/SiO₂ catalysts. Energy Environ. Sci. 3(3), 328–333 (2010). doi:10.1039/B923795J
- A.V. Anisimov, A.V. Tarakanova, Oxidative desulfurization of hydrocarbon raw materials. Russ. J. Gen. Chem. 79(6), 1264–1273 (2009). doi:10.1134/S1070363209060437
- J.M. Campos-Martin, M.C. Capel-Sanchez, P. Perez-Presas, J.L.G. Fierro, Oxidative processes of desulfurization of liquid fuels. J. Chem. Technol. Biotechnol. 85(7), 879–890 (2010). doi:10.1002/ jctb.2371
- F-t Li, R-h Liu, W. Jin-hua, D-s Zhao, Z-m Sun, Y. Liu, Desulfurization of dibenzothiophene by chemical oxidation and solvent extraction with Me₃NCH₂C₆H₅Cl-2ZnCl₂ ionic liquid. Green Chem. 11(6), 883–888 (2009). doi:10.1039/B815575E

- Y. Shiraishi, T. Hirai, I. Komasawa, TiO₂-mediated photocatalytic desulfurization process for light oils using an organic two-phase system. J. Chem. Eng. Jpn. 35(5), 489–492 (2002)
- R. Vargas, O. Núñez, The photocatalytic oxidation of dibenzothiophene (DBT). J. Mol. Catal. A 294(1–2), 74–81 (2008). doi:10.1016/j.molcata.2008.08.001
- R. Vargas, O. Núñez, Photocatalytic degradation of oil industry hydrocarbons models at laboratory and at pilot-plant scale. Sol. Energy 84(2), 345–351 (2010). doi:10.1016/j.solener.2009.12.005
- A. Fujishima, T.N. Rao, D.A. Tryk, Titanium dioxide photocatalysis. J. Photochem. Photobiol. C 1(1), 1–21 (2000). doi:10.1016/S1389-5567(00)00002-2
- 15. M. Anpo, Preparation, characterization, and reactivities of highly functional titanium oxide-based photocatalysts able to operate under UV–Vis light irradiation: approaches in realizing high efficiency in the use of visible light. Bull. Chem. Soc. Jpn. 77(8), 1427–1442 (2004)
- A.L. Linsebigler, G. Lu, J.T. Yates, Photocatalysis on TiO₂ surfaces: principles, mechanisms, and selected results. Chem. Rev. 95(3), 735–758 (1995). doi:10.1021/cr00035a013
- I. Salem, Recent studies on the catalytic activity of titanium, zirconium, and hafnium oxides. Catal. Rev. 45(2), 205–296 (2003). doi:10.1081/CR-120015740
- A. Selvaraj, S. Sivakumar, A.K. Ramasamy, V. Balasubramanian, Photocatalytic degradation of triazine dyes over N-doped TiO₂ in solar radiation. Res. Chem. Intermed. **39**(6), 2287–2302 (2013). doi:10.1007/s11164-012-0756-x
- S. Matsuzawa, J. Tanaka, S. Sato, T. Ibusuki, Photocatalytic oxidation of dibenzothiophenes in acetonitrile using TiO₂: effect of hydrogen peroxide and ultrasound irradiation. J. Photochem. Photobiol. A 149(1–3), 183–189 (2002). doi:10.1016/S1010-6030(02)00004-7
- J. Robertson, T.J. Bandosz, Photooxidation of dibenzothiophene on TiO₂/hectorite thin films layered catalyst. J. Colloid Interface Sci. 299(1), 125–135 (2006). doi:10.1016/j.jcis.2006.02.011
- D. Zhao, J. Zhang, J. Wang, W. Liang, H. Li, Photocatalytic oxidation desulfurization of diesel oil using Ti-containing Zeolite. Pet. Sci. Technol. 27(1), 1–11 (2009). doi:10.1080/10916460802108314
- 22. B. Ohtani, Preparing articles on photocatalysis—beyond the illusions, misconceptions, and speculation. Chem. Lett. **37**(3), 217–229 (2008)
- T. Sano, N. Negishi, K. Koike, K. Takeuchi, S. Matsuzawa, Preparation of a visible light-responsive photocatalyst from a complex of Ti⁴⁺ with a nitrogen-containing ligand. J. Mater. Chem. 14(3), 380–384 (2004). doi:10.1039/B311444A
- 24. Y.-B. Tang, C.-S. Lee, J. Xu, Z.-T. Liu, Z.-H. Chen, Z. He, Y.-L. Cao, G. Yuan, H. Song, L. Chen, L. Luo, H.-M. Cheng, W.-J. Zhang, I. Bello, S.-T. Lee, Incorporation of graphenes in nanostructured TiO₂ films via molecular grafting for dye-sensitized solar cell application. ACS Nano 4(6), 3482–3488 (2010). doi:10.1021/nn100449w
- H. Li, X. He, Z. Kang, H. Huang, Y. Liu, J. Liu, S. Lian, C.H.A. Tsang, X. Yang, S.-T. Lee, Watersoluble fluorescent carbon quantum dots and photocatalyst design. Angew. Chem. Int. Ed. 49(26), 4430–4434 (2010). doi:10.1002/anie.200906154
- H. Zuo, J. Sun, K. Deng, R. Su, F. Wei, D. Wang, Preparation and characterization of Bi³⁺-TiO2 and its photocatalytic activity. Chem. Eng. Technol. 30(5), 577–582 (2007). doi:10.1002/ceat.200700022
- J. Ma, Y. Wei, W.-X. Liu, W.-B. Cao, Preparation of nanocrystalline Fe-doped TiO₂ powders as a visible-light-responsive photocatalyst. Res. Chem. Intermed. 35(3), 329–336 (2009). doi:10.1007/ s11164-009-0027-7
- R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, Y. Taga, Visible-light photocatalysis in nitrogen-doped titanium oxides. Science 293(5528), 269–271 (2001). doi:10.1126/science.1061051
- P. Periyat, S.C. Pillai, D.E. McCormack, J. Colreavy, S.J. Hinder, Improved high-temperature stability and sun-light-driven photocatalytic activity of sulfur-doped anatase TiO₂. J Phys Chem C 112(20), 7644–7652 (2008). doi:10.1021/jp0774847
- S. Sakthivel, H. Kisch, Daylight photocatalysis by carbon-modified titanium dioxide. Angew. Chem. Int. Ed. 42(40), 4908–4911 (2003). doi:10.1002/anie.200351577
- M. Adams, N. Skillen, C. McCullagh, P.K.J. Robertson, Development of a doped titania immobilised thin film multi tubular photoreactor. Appl. Catal. B 130–131, 99–105 (2013). doi:10.1016/j.apcatb. 2012.10.008
- 32. C.-H. Zhou, X.-Z. Zhao, B.-C. Yang, D. Zhang, Z.-Y. Li, K.-C. Zhou, Effect of poly (ethylene glycol) on coarsening dynamics of titanium dioxide nanocrystallites in hydrothermal reaction and the application in dye sensitized solar cells. J. Colloid Interface Sci. 374(1), 9–17 (2012). doi:10.1016/j. jcis.2011.12.006

- 33. L.C.-K. Liau, H. Chang, T.C.-K. Yang, C.-L. Huang, Effect of poly(ethylene glycol) additives on the photocatalytic activity of TiO₂ films prepared by sol–gel processing and low temperature treatments. J. Chin. Inst. Chem. Eng, **39**(3), 237–242 (2008). doi:10.1016/j.jcice.2007.12.014
- 34. H. Chang, E.-H. Jo, H.D. Jang, T.-O. Kim, Synthesis of PEG-modified TiO₂–InVO₄ nanoparticles via combustion method and photocatalytic degradation of methylene blue. Mater. Lett. **92**, 202–205 (2013). doi:10.1016/j.matlet.2012.11.006
- 35. F. Deng, Y. Li, X. Luo, L. Yang, X. Tu, Preparation of conductive polypyrrole/TiO₂ nanocomposite via surface molecular imprinting technique and its photocatalytic activity under simulated solar light irradiation. Colloids Surf. A. 183–189 (2012). doi:10.1016/j.colsurfa.2011.12.029.
- 36. D. Wang, Y. Duan, Q. Luo, X. Li, J. An, L. Bao, L. Shi, Novel preparation method for a new visible light photocatalyst: mesoporous TiO₂ supported Ag/AgBr. J. Mater. Chem. 22, 4847–4854 (2012). doi:10.1039/C2JM14628B
- S.X. Luo, F.M. Wang, Z.S. Shi, F. Xin, Preparation and photocatalytic activity of Zr doped TiO₂. Mater. Res. Innov. 13(1), 64–69 (2009). doi:10.1179/143307509X402219
- D. Li, H. Haneda, S. Hishita, N. Ohashi, Visible-light-driven nitrogen-doped TiO₂ photocatalysts: effect of nitrogen precursors on their photocatalysis for decomposition of gas-phase organic pollutants. Mater. Sci. Eng. B **117**(1), 67–75 (2005). doi:10.1016/j.mseb.2004.10.018
- 39. J.-G. Yu, H.-G. Yu, B. Cheng, X.-J. Zhao, J.C. Yu, W.-K. Ho, The effect of calcination temperature on the surface microstructure and photocatalytic activity of TiO₂ thin films prepared by liquid phase deposition. J. Phys. Chem. B **107**(50), 13871–13879 (2003). doi:10.1021/jp036158y
- A. Hinchliffe, N. Trinajstic, Calculation of proton coupling constants for dibenzothiophene radical anion. Theor. Chim. Acta (Berl.) 10, 458–460 (1968). doi:10.1007/BF00528777
- N. Daneshvar, D. Salari, A.R. Khataee, Photocatalytic degradation of azo dye acid red 14 in water on ZnO as an alternative catalyst to TiO₂. J. Photochem. Photobiol. A **162**(2–3), 317–322 (2004). doi:10. 1016/S1010-6030(03)00378-2
- 42. M. Pérez, F. Torrades, J.A. García-Hortal, X. Domènech, J. Peral, Removal of organic contaminants in paper pulp treatment effluents under Fenton and photo-Fenton conditions. Appl. Catal. B 36(1), 63–74 (2002). doi:10.1016/S0926-3373(01)00281-8
- C.S. Turchi, D.F. Ollis, Photocatalytic degradation of organic water contaminants: mechanisms involving hydroxyl radical attack. J. Catal. **122**(1), 178–192 (1990). doi:10.1016/0021-9517(90)90269-P
- 44. J.-M. Herrmann, Heterogeneous photocatalysis: fundamentals and applications to the removal of various types of aqueous pollutants. Catal. Today **53**(1), 115–129 (1999). doi:10.1016/S0920-5861(99)00107-8
- 45. W. Boyles, The Science of Chemical Oxygen Demand, Technical Information Series, Booklet No. 9, (Hach, Loveland, 1997)