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Different effects of humic substances on photodegradation of p,p'-DDT on soil surfaces in the presence of TiO$_2$ under UV and visible light

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Abstract

Different effects of humic substances (HS) on TiO$_2$ photocatalytic degradation of p,p'-DDT on soil surfaces were observed under the irradiation of UV and visible light. Under UV light irradiation, HS inhibited the photodegradation of p,p'-DDT on natural soil surfaces as well as photocatalytic degradation induced by TiO$_2$. The decrease of UV-Vis absorbance values and total organic carbon indicated that HS underwent degradation and were mineralized in the presence of TiO$_2$. The adsorption of 2 wt.% HS onto TiO$_2$ extend the response of TiO$_2$ to visible light evidenced by the UV-Vis diffuse reflectance spectra. Under visible light irradiation, p,p'-DDT degradation on HS-sensitized TiO$_2$ was observed. By injecting electrons from the photoexcited HS to the conduction band of TiO$_2$, the sensitized TiO$_2$ degraded p,p'-DDT under the irradiation of visible light. In addition, photodegradation of p,p'-DDT was accelerated in the presence of HS. On the analysis of photoproducts using a gas chromatography coupled with a mass spectrometer analysis, DDE and DDD were detected under irradiation of UV light. It is suggested that DDE could be produced by active radicals and the produced DDD may be due to direct photodegradation of p,p'-DDT. Under irradiation of visible light, produced electrons by photosensitization reaction could attack the aliphatic Cl of p,p'-DDT, leading to the production of DDD. The different photoproducts further confirmed that different mechanism of p,p'-DDT photodegradation was involved under irradiation of UV and visible light.

1. Introduction

Humic substances (HS) or natural organic matter, widespread existing in water or soil environment systems, are heterogeneous mixtures of a variety of organic compounds, consisting of aromatic, aliphatic, phenolic, and quinolic functional groups with varying molecular sizes and properties [1]. Dissolved organic matter can either enhance [2,3] or inhibit [4,5] the rate of photodegradation of organic contaminants in aqueous solutions. Consequently, it is important to investigate the effect of HS on photodegradation of organic contaminants on soil surfaces.

The photocatalytic degradation of organic pollutants using TiO$_2$ has demonstrated successful performance in various remediation systems of polluted water and air [6]. Therefore, it is worthwhile to study the photocatalytic reaction occurring on soil–air surfaces. Although TiO$_2$ is very popular as a photocatalyst, it suffers from the lack of visible

light absorption. This practically limits the utility of sunlight as energy source for the degradation because significant part of the solar energy reaching the earth surface lies in the visible and near infrared region of spectrum. An important way to extend the response of the TiO$_2$ is by photosensitization. Photosensitization is the application of organic or inorganic chromophores to extend the spectral response of a photochemical process. Various organic and inorganic dyes/photosensitizers have been demonstrated to be able to effect charge injection efficiently into the semiconductor upon excitation by with less than bandgap energy photons [7]. HS with strong and wide absorbing properties were used as photosensitizer in exciting ZnO photocatalyst under irradiation of visible light [8]. Most of the recent studies on photosensitizer–semiconductor systems concern the direct light-to-electricity and light-to-chemical-fuels conversion by photoelectrochemical cells. Surprisingly little effort has been spent on the application of photosensitizers to enhance the efficiency of photodegradation processes [9].

In the current work, the HS-sensitized TiO$_2$ photocatalytic degradation of p,p'-DDT on soil surfaces was investigated mainly under irradiation of visible light. Under UV

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irradiation, the role of HS in TiO₂ photocatalytic degradation of *p,p′*-DDT on soil surfaces was also investigated. In addition, the effect of HS on *p,p′*-DDT photodegradation on natural soil surfaces under irradiation of UV and visible light was further examined. The degradation products of *p,p′*-DDT were identified by a gas chromatography coupled with a mass spectrometer (GC–MS). *p,p′*-DDT was selected as probe compound because it belongs to persistent organic contaminants and its pollution is still heavy [10].

2. Experimental

2.1. Materials

p,p′-DDT, *p,p′*-DDE, and *p,p′*-DDD (ACS reagent grade, purity ≥ 99.0%) were purchased from the National Environmental Monitoring Station of China and used as received. Hexane and acetone (HPLC/SPECTRO grade) were purchased from Tedia (USA). TiO₂ (chemical purity) was obtained from the Beijing Chemical Company. Its crystalline is anatase as confirmed by the X-ray diffraction analysis using Shimadzu LabX XRD-6000 X-ray diffractometer. Surface soil samples (0–2 cm) were collected from an agricultural field in the suburb of Dalian, China. After being air-dried, soil samples were passed though a 0.22 mm sieve, and stored in dark before use. This soil was chosen because it had the relatively low TOC and it was reasoned that this soil would be most likely to show effects of exogenously added HS. Its characteristics are as follows: the contents of sand, silt, clay, and organic matter content are 46.7, 37.5, 15.8, and 0.25%, respectively; density 2.49 g/cm³; pH 8.2. HS was extracted from soils using the method described by Zepp et al. [11]. Contents of C, H, N, and ash fraction were 43.12, 3.42, 1.27, and 0.56%, respectively as determined by combustion analysis using a Perkin-Elmer 2400 CHN elemental analyzer.

2.2. Preparation of HS/TiO₂ powder

The solutions of HS (100 mg/1) were prepared by dissolving 2 mg of HS in 20 ml of pure water (Milli-Q device, Millipore) buffered at pH 6.5 with phosphates. The solutions were stirred until the complete dissolution of the humic material and filtered on 0.45 μm Millipore cellulose filters prior to use. Filtration led only small losses of material. The filtrate was stored as an HS stock solution and its concentration was checked by measuring the TOC value. Given amounts of TiO₂ were added into certain volume of HS solutions. The adsorption of HS onto TiO₂ was achieved by shaking the suspension of HS and TiO₂ at a shaker for 5 h. The suspension was filtrated on 0.45 μm Millipore cellulose filters. The filtrate was checked using TOC analyzer for determining the amount of adsorbed HS on TiO₂. Following, TiO₂ with adsorbed HS were dried at 50 °C. The optical absorption spectra of TiO₂ and HS/TiO₂ powder were recorded with an UV-Vis spectrophotometer
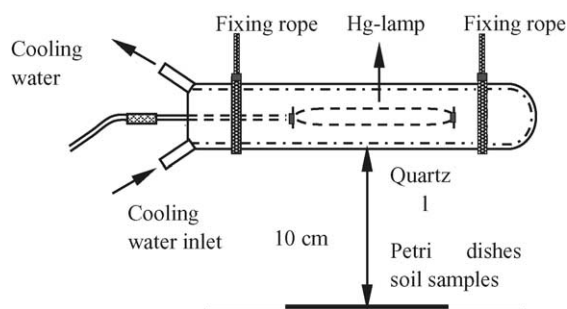

Fig. 1. Schematic experimental device for the photodegradation experiment.

with a diffuse reflectance attachment. Scanning electron microscopic (SEM) was used to observe its profile.

2.3. Photodegradation of p,p′-DDT under UV light irradiation

Adsorption of *p,p′*-DDT to the soil samples was accomplished by spiking *p,p′*-DDT (dissolved in petroleum ether) into the soils and evaporating to dryness. The concentration of *p,p′*-DDT was determined to be 1234 ng/g (*p,p′*-DDT/soils). The amount of soil sample spiked with *p,p′*-DDT that are spread onto the Petri dishes are kept to be 1.0 ± 0.1 g. After being photoirradiated, the soil samples were transferred into 50 ml glass bottle and weighted for further analysis.

The experiment device consists of a climate chamber and a lighting system. The lighting system included a 300 W high-pressure mercury lamp (GGZ 300, Phillips, maximum wavelengths 254, 265 302, 313, and 365 nm) and a quartz immersion well with circulating water, as shown in Fig. 1. Soil samples contained in the Petri dish (10 cm diameter) were placed 10 cm below the lamp. The temperature in the chamber was adjusted to 25 ± 1 °C. During different intervals of exposure, three duplicate samples were taken out from the chamber and transferred into 50 ml bottles. Dark control samples covered by aluminum foil were included to evaluate the contribution of nonphotolysis factors to dissipation of *p,p′*-DDT.

2.4. Photodegradation of p,p′-DDT on visible light irradiation

The photochemical experiment under irradiation of visible light was performed in an artificial climate incubator (HPG-280H) that was purchased from Harbin Donglian Electronic & Technology Development Co., Ltd., China. Fluorescent lamp (30 W × 12) was used as light source. A Humidifier (20 W) was used to control the humidity. The temperature and humidity inside the incubator were kept to be 20 °C and 65%, respectively, which were adjusted by dry and wet bulb dual temperature control. The photodegradation experiment was carried out in the similar way as the

method described in Section 2.3 except for the different irradiation periods.

2.5. Analysis methods

The soil samples were transferred into 50 ml glass bottles, and mixed with 20 ml mixtures of acetone and hexane (1:1, v/v). After being shaken for 1 h (300 rpm) in a shaker, each sample was extracted for 30 min in an ultrasonic bath. The mixtures were then centrifuged at 5000 rpm for 15 min to separate the supernatant from the soil. The supernatant was cleaned with 50 ml of deionized water twice. Then, the extract was concentrated to 2 ml by a gentle stream of nitrogen (N_2) and passed though a glass column (i.d. = 8 mm) containing 3 g of activated florisil topped with 1 g anhydrous Na_2SO_4. The extracts were eluted with 5 ml mixture of hexane: acetone (95:5, v/v) and 5 ml hexane in turn. After being dehydrated with Na_2SO_4, the eluted extracts were reduced to 2 ml under a gentle N_2 stream. The extraction recovery of p,p'-DDT under given conditions was greater than 95%. For quantification, the extracts were analyzed by HP 6890 GC equipped with a ^{63}Ni electron capture detector. The operating temperature of the injector and detector was 250 and 280 °C, respectively. The oven temperature of GC was programmed from 130 to 240 °C at a ramp rate of 20 °C/min. The hold time at 130 and 240 °C was 1.00 and 2.00 min, respectively. Helium gas was used as carrier gas with a flow of 1.0 ml/min. The GC was calibrated daily with external standard samples; duplicate measurements were made for each sample with an injection (splitless) volume of 1 μl. In order to identify intermediate products, the extracts were analyzed using GC (HP6890) with a capillary column (HP5) coupled with a MS (HP5973). The injector temperature was 250 °C; the source temperature of MS detector was 230 °C. A solvent delay was set to 4 min. The oven temperature was programmed from 60 to 260 °C (20 min) at a ramp rate of 15 °C/min.

For the experiment on analyzing the change of HS during photoirradiation process, soil samples at different photoirradiation time were transferred into 150 mL glass bottles, mixed with 50 mL NaOH (0.1 M) solution, and shaken for 3 h to desorb HS from soil particles. Then, the mixtures were centrifuged at 8000 rpm for 15 min and the supernatant obtained was used for further analysis. The UV-Vis absorption spectra of the supernatant at different times were recorded using a UV/Vis Spectrophotometer (Jasco V-550, Japan) and the TOC values were measured using a Shimadzu TOC analyzer.

3. Results and discussion

3.1. Photosensitized degradation of p,p′-DDT under irradiation of visible light

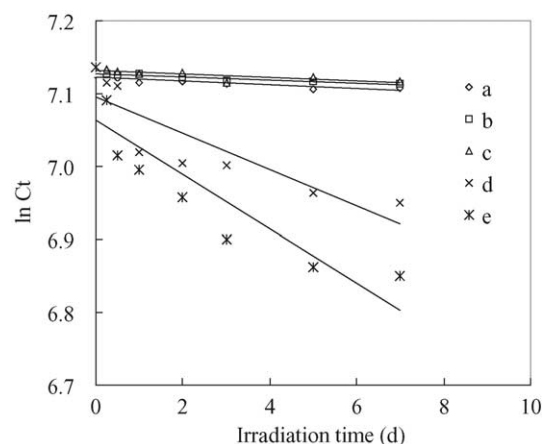Several experimental results indicated that the photodegradation rates of various organic contaminants

Fig. 2. HS induced photosensitization degradation of p,p'-DDT on soil surfaces in the presence of TiO_2 under irradiation of visible light: (a) dark control; (b) natural soils; (c) 2 wt.% TiO_2; (d) 2 wt.% HS; (e) 2 wt.% HS/TiO_2 and 2 wt.% HS.

fitted the Langmuir–Hinshelwood model [12]. The Langmuir–Hinshelwood rate form is

$$v = \frac{dC}{dt} = \frac{kKC}{1 + KC} \tag{1}$$

where v is the reaction rate of the reactant, C the concentration of the reactant, t the illumination time, k the reaction rate constant, and K the adsorption coefficient. Integration of Eq. (1) yield Eq. (2):

$$\ln\left(\frac{C_0}{C}\right) + K(C_0 - C) = kKt \tag{2}$$

When the initial concentration C_0 is low, Eq. (2) is altered to Eq. (3):

$$\ln\left(\frac{C_0}{C}\right) = kKt = k_{tot}t \tag{3}$$

which express pseudo-first-order reactions, where k_{tot} is the apparent photodegradation rate constant. The photodegradation kinetic curves of p,p'-DDT on the soil surfaces under visible light irradiation are presented in Fig. 2. The values of k_{tot} and the linear regression coefficients for the pseudo-first-order kinetics of the p,p'-DDT degradation are listed in Table 1. According to these results, the photodegradation kinetics of p,p'-DDT with the concentration of 1234 ng/g adsorbed onto soil particles follows a

Table 1
Kinetic parameters for the photodegradation of p,p'-DDT on soil surfaces under irradiation of visible light

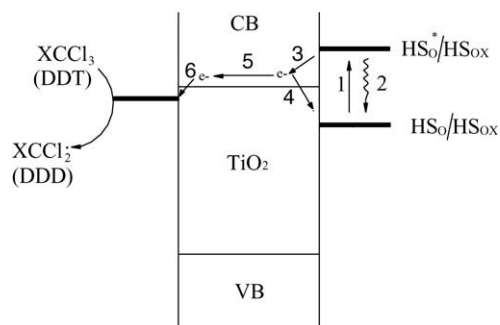| Photoreactive conditions	k_T (day^{-1})	r	$t_{1/2}$ (days)
Dark control	0.0024	0.809	288.75
Natural soil samples	0.0023	0.970	301.30
2 wt.% TiO_2	0.0025	0.966	277.20
2 wt.% HS	0.0250	0.877	27.72
2 wt.% HS/TiO_2 and 2 wt.% HS	0.0371	0.898	18.68

Fig. 3. Visible light-induced degradation of DDT on soil surfaces by HS/TiO$_2$ system. HS$_0$ stands for ground-state HS molecules; HS*, electronically excited HS; HSox, oxidized HS. The numbers represent the primary electronic pathways in photosensitization: 1—excitation of HS; 2—fluorescent decay of HS; 3—electron injection from excited HS into CB; 4—back electron transfer to HSox; 5—electron migration within the lattice onto the surface; 6—electron transfer to p,p'-DDT.

Fig. 4. UV-Vis diffuse reflectance spectra of bare TiO$_2$ and HS/TiO$_2$ (2 wt.%) powders.

pseudo-first-order degradation curve, which is consistent to the Langmuir–Hinshelwood model.

Quantitative recoveries from dark controls sampled over the entire exposure period of visible light irradiation showed that p,p'-DDT was very stable (Fig. 2), indicating the loss of p,p'-DDT owed to volatilization and biodegradation can be ignored. In the presence of 2 wt.% TiO$_2$, no degradation of p,p'-DDT was observed. While, in the presence of 2 wt.% HS, apparent degradation of p,p'-DDT was observed and the degradation half-life was 27.72 days as listed in Table 1. Furthermore, faster degradation of p,p'-DDT in the presence of 2 wt.% HS/TiO$_2$ and 2 wt.% HS was observed, and the degradation half-life was reduced to 18.68 days.

HS are polymeric oxidation products that result from the decomposition of plant and animal residues. It can act as photosensitizers by the absorption of sunlight of a wavelength range of 290 nm to visible light and the subsequent formation of highly reactive molecules like hydroxy-radicals, singlet oxygen or H$_2$O$_2$ [13]. The first step required for HS-mediated photochemical reactions is the excitation of humic substances by light. Subsequently, physical processes and/or chemical reactions follow and finally the HS molecule returns to its ground state or stable products are formed. The formation of reactive species can indirectly lead to transformations of photochemically inert pollutants [14,15]. Because p,p'-DDT is photochemically inert under irradiation of visible light, the degradation of p,p'-DDT in the presence of HS is believed to be induced by the added HS.

Photosensitization is widely used to extend the photoresponse of TiO$_2$ into the visible region. The principle of photosensitization of TiO$_2$ is illustrated in Fig. 3 that indicates the primary electron pathways. The visible light excites the sensitizer molecules adsorbed on TiO$_2$ and subsequently inject electrons to conduction band (CB) of TiO$_2$. While the CB acts as a mediator for transferring electrons from the sensitizer to substrate electron acceptors on TiO$_2$ surface,
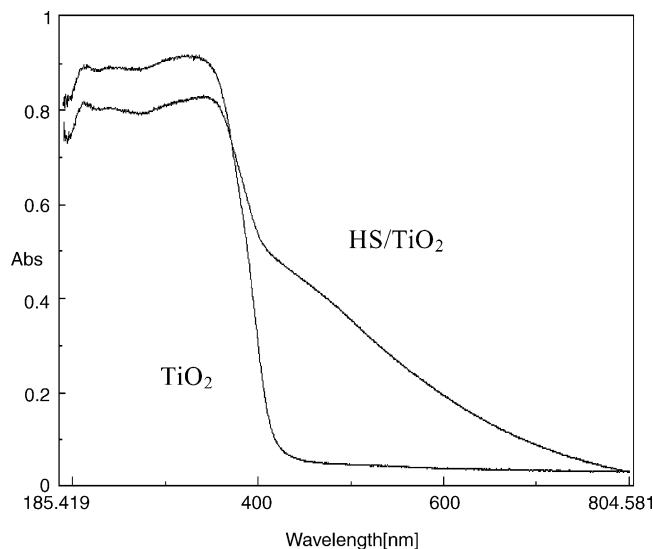
the valence band (VB) remains unaffected in a typical photosensitization. The oxidized photosensitizer can be regenerated by suitable sacrificial electron donor. In our case, the mass proportion of adsorbed HS to TiO$_2$ is determined to be 2% by TOC analyzer. Fig. 4 compares the diffuse reflectance spectrum of the sensitized TiO$_2$ with that of pure TiO$_2$ powder. The absorbance of HS/TiO$_2$ powder was extended compared to the pure TiO$_2$ powder. Based on the SEM results of Figs. 5 and 6, it is observed that HS coated TiO$_2$ particles. The ability of fulvic acid to sensitize colloidal ZnO has been demonstrated by fluorescence emission and transient absorption measurements in a mixed alcohol–water mixture [8]. By visible light irradiation, long-lived electrons can be trapped at the semiconductor surface and utilized as charge carriers for the reduction of pollutants and other substrates. In addition, study has already demonstrated that initial re-
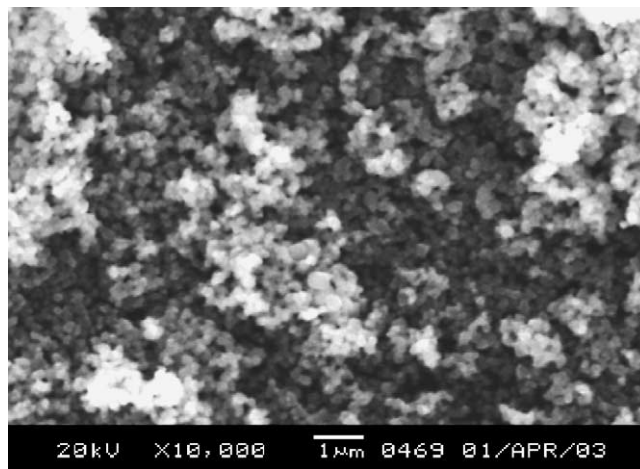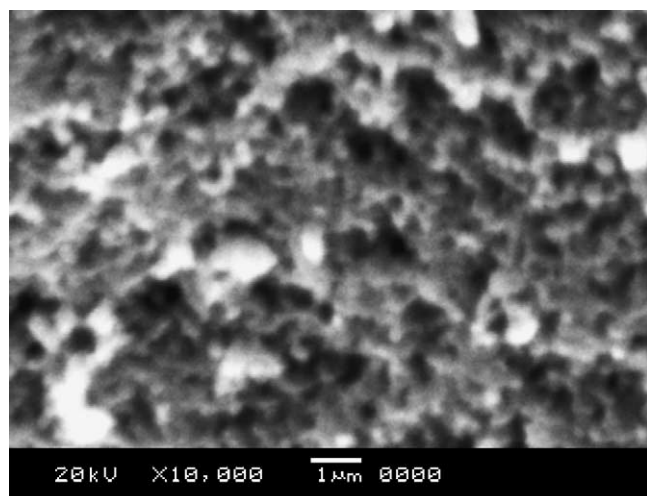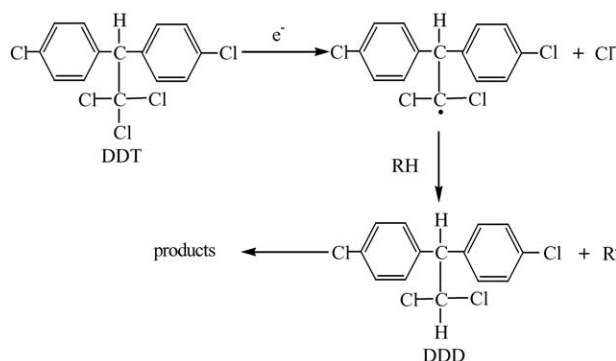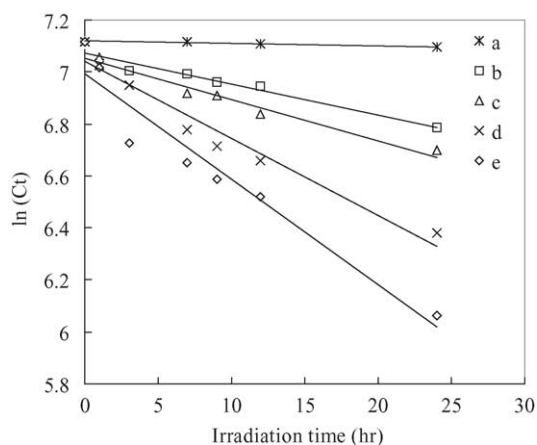

Fig. 5. SEM image of bare TiO$_2$ powder.

Fig. 6. SEM image of HS/TiO$_2$ (2 wt.%) powder.

Table 2
Kinetic parameters for the photodegradation of p,p'-DDT on soil surfaces under irradiation of UV light

Photoreactive conditions	k_T (day^{-1})	r	$t_{1/2}$ (h)
Dark control	0.0009	0.962	770.0
Natural soil samples	0.0297	0.979	23.3
2 wt.% HS	0.0118	0.966	58.7
2 wt.% TiO$_2$	0.0405	0.966	17.1
2 wt.% HS/TiO$_2$ and 2 wt.% HS	0.0158	0.951	43.9

duction steps were involved in the degradation of CCl$_4$ by TiO$_2$ [7,16]. Consequently, it is suggested that the electrons injected into the conduction band of TiO$_2$ by visible irradiation should be able to initiate reductive dechlorination of aliphatic Cl of p,p'-DDT. By GC–MS analysis, DDD was identified and its formation process is presented in Fig. 7. This result further confirmed the photoreduction pathway of p,p'-DDT degradation by HS/TiO$_2$ under irradiation of visible light.
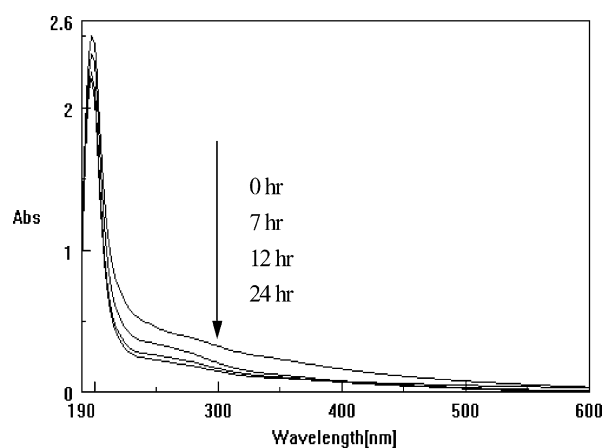

Fig. 7. Proposed photosensitized reaction for the formation of DDD in the presence of 2 wt.% HS/TiO$_2$ and 2 wt.% HS powder under visible light irradiation.

Fig. 9. Variations of UV-Vis absorbance spectrum of HS desorbed from soil samples at different times.

Fig. 8. Effects of HS on the photodegradation of p,p'-DDT on soil surfaces in the presence of TiO$_2$ under irradiation of UV light: (a) dark control; (b) 2 wt.% HS; (c) 2 wt.% HS/TiO$_2$ and 2 wt.% HS; (d) natural soils; (e) 2 wt.% TiO$_2$.
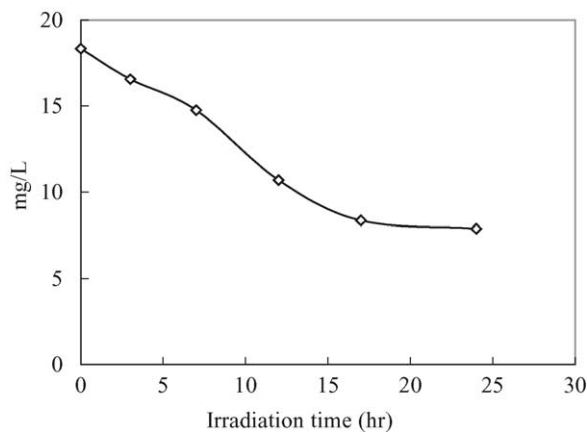

Fig. 10. Variations of total organic carbon from HS that were desorbed into aqueous solution (1000 mL) from soil samples at different photoirradiation times.
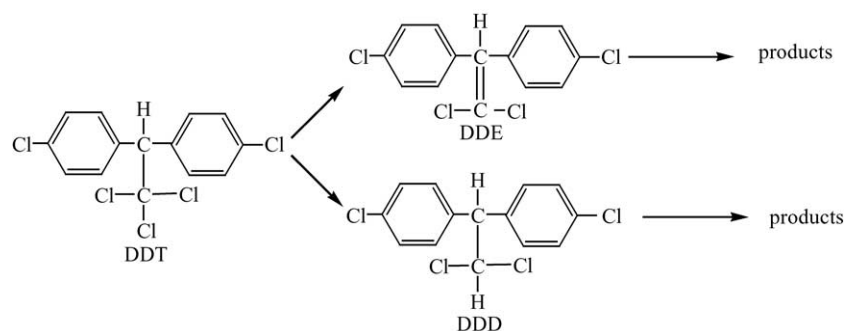
Fig. 11. Proposed photodegradation pathway of p,p'-DDT on soil surfaces under UV light irradiation.

3.2. Photodegradation of p,p'-DDT under irradiation of UV light

The p,p'-DDT photodegradation under UV light irradiation follow identical pseudo-first-order kinetics. The kinetic plots are presented in Fig. 8. On natural soil surfaces, p,p'-DDT undertook photodegradation with a kinetic constant of $0.0297\,h^{-1}$ as listed in Table 2. p,p'-DDT is photoactive under irradiation of UV light. In addition, some studies have already indicated that certain amounts of semiconducting substances such as iron and titanium oxides in the soils may lead to photocatalytic degradation of γ-HCH under irradiation of UV light [17,18]. Therefore, direct photodegradation or photocatalytic degradation may contribute to the degradation of p,p'-DDT. The addition of 2 wt.% TiO$_2$ accelerated the photodegradation of p,p'-DDT largely, increasing the first-order kinetic constant to $0.0405\,h^{-1}$. Conduction band electrons and valence band holes are generated when TiO$_2$ is irradiated with light energy greater than its bandgap energy (3.2 eV). The photogenerated electrons could reduce the organic compounds or react with electron acceptors such as O$_2$, reducing it to superoxide radical anion O$_2^-$. The photogenerated holes can oxidize either the organic molecule directly, or the OH$^-$ ions and the H$_2$O molecules adsorbed at the TiO$_2$ surface, to OH$^\bullet$ radicals [6]. All of these produced active radicals may be responsible for the enhanced photodegradation of p,p'-DDT.

The addition of 2 wt.% HS inhibited the p,p'-DDT photodegradation in natural soils. The pseudo-first-order rate constant was reduced from 0.0297 to $0.0118\,h^{-1}$, as listed in Table 2. The decrease of p,p'-DDT photodegradation rate constants could be due to the shielding effect, which protects them from incident radiation. In addition, HS may absorb most of the photons emitted thereby slowing down direct photodegradation of p,p'-DDT. Another reason may be that HS quench the excited states of p,p'-DDT, thus retarding the photodegradation.

Effect of HS on the photocatalytic degradation of p,p'-DDT in the presence of TiO$_2$ was further studied by spiking 2 wt.% HS/TiO$_2$ and 2 wt.% HS powder into soils together. As listed in Table 2, the photocatalytic degradation rate of p,p'-DDT in the presence of 2 wt.% HS/TiO$_2$ and

2 wt.% HS was reduced from 0.0405 to $0.0158\,h^{-1}$. The UV-Vis absorbance values and decreased TOC values of HS solution with the evolution of irradiation time were observed which are presented in Figs. 9 and 10, respectively. The above results indicate that HS were degraded and mineralized partially during the photoirradiation. This process can be contributed to either direct photolysis or photocatalytic degradation induced by TiO$_2$. The direct photolysis can reduce the light available to attack the p,p'-DDT molecules or to excite the TiO$_2$; the photocatalytic degradation of HS could consume active radicals produced by TiO$_2$. Both processes may contribute to the retarding effect of HS on the TiO$_2$ photocatalytic degradation of p,p'-DDT. Under UV light irradiation, DDE and DDD were detected by GC–MS. The degradation pathway of p,p'-DDT under UV irradiation is presented in Fig. 11. The different photodegradation intermediates and pathways suggested different degradation mechanisms were involved under irradiation of UV and visible light irradiation.

4. Conclusions

Different effects of HS on photodegradation of p,p'-DDT on soil surfaces in the presence of TiO$_2$ are involved under UV and visible light irradiation. According to our experiments, the rapid photocatalytic or direct photodegradation of p,p'-DDT initiated by the UV-radiation will be retarded by the presence of the HS. On the other hand, visible light-induced degradation of p,p'-DDT on HS-sensitized TiO$_2$ was observed. It is suggested that the electrons produced by excited HS injected into the conduction band of TiO$_2$ by visible irradiation should be able to initiate reductive dechlorination of p,p'-DDT. In addition, an indirect, HS-mediated process will lead to the relatively slow, visible light-initiated photodegradation of p,p'-DDT. The mechanism of p,p'-DDT photodegradation under irradiation of UV light and visible light is clearly different as indicated by the fact that the photoproducts are distinct. Under UV light irradiation, DDD and DDE are produced through dechlorination and dehydrochlorination, whereas photosensitized reaction induced by visible light yields DDD.

Acknowledgements

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