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Photodegradation of γ-HCH by α-Fe_2O_3 and the influence of fulvic acid

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Abstract

The purpose of this study was to examine photodegradation of γ-hexachlorocyclohexane (γ-HCH) by α-Fe_2O_3 and the influence of fulvic acid (FA) in this photochemical process. A 300 W high-pressure mercury lamp was employed as the light source. The result showed that the UV light alone could play an important role in the degradation of γ-HCH. The presence of α-Fe_2O_3 was found to promote the photodegradation of γ-HCH. The photodegradation of γ-HCH by α-Fe_2O_3 follows pseudo-first-order reaction kinetics. The effect of the FA on the photodegradation of γ-HCH was also performed. The result revealed that the FA slowed the photodegradation rate of γ-HCH. Oxidation products were also identified by gas chromatography with a mass spectroscopy detector. This process is of interest in both a remedial process induced by iron oxides in natural water surfaces and α-Fe_2O_3-mediated photodegradation method for purifying natural water containing γ-HCH and humic substances.

Keywords: α-Fe_2O_3; γ-HCH; Fulvic acid; Photodegradation; Humic substances

1. Introduction

Over the last decades, the role of photochemical reactions at suspended semiconducting granules in natural water has been postulated to be significant in modifying the transformation processes of environmental pollutants [1–3]. It is well known that iron oxides exist widely in nature, and most of iron oxides have been revealed the photochemical active [4]. Our recent work displayed that total iron contents in soil have remarkable catalysis on photodegradation of γ-HCH. The positive correlation was found between iron contents and the photodegradation rate constant of γ-HCH [5]. In aquatic systems, Fe-rich particles have been recognized for decades as ubiquitous constitutes. Although iron oxides have poor efficiency and are not stable in acidic media, we might expect that photochemical reactions involved by iron oxides are ubiquitous in natural water due to their widespread existence [6].

The photolysis of aquatic organic contaminants can be influenced by the presence of humic substance (HS) in several ways. On one hand, direct photolysis can be inhibited by colored HS because of the competitive absorption for available light [7,8]. On the other hand, ultraviolet irradiation also induces a variety of photochemical changes in HS and leads to production of reactive oxygen species (e.g., singlet oxygen, peroxy radicals) [9,10]. These reactive chemical species could oxidize the organic contaminants. Owing to the twofold role of HS, photochemical fate of chemical contaminants in the presence of HS may differ significantly. Therefore, there is a need to expand the number of organic pollutants whose photodegradation are examined in the presence of HS. To the best our knowledge, there is little information about the effect of HS on the photodegradation of γ-HCH.

Both iron oxides and HS are the prevalent constituent of natural water. A thorough investigation of photodegradation of environmental chemicals by iron oxides in the presence of HS is warranted. These studies are important for understanding remedial process occurring in natural water surface.

Organochlorine compounds constitute an important category of water pollutants. Among these, γ-HCH marketed

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under the generic name of lindane, had been most extensively applied to control many leaf-eating insects throughout the world during last century [11,12]. Because of its toxicity and non-biodegradation when released in the environment, most countries have restricted its use. Even so, the past decade or more saw the existence of γ-HCH in the surface of water in many countries [13]. Recently, studies have shown γ-HCH can cause a severe ecological problem [14].

So far, only a few studies in a laboratory scale have been reported on the photochemical degradation of γ-HCH mediated by TiO_2 [15,16]. There is a dearth of information concerning photodegradation of γ-HCH catalyzed by iron oxides. The aim of the present work was to observe the photodegradation of γ-HCH in the presence of α-Fe_2O_3. The role of HS in this photochemical process was also elucidated.

2. Experimental

2.1. Materials

α-Fe_2O_3 was synthesized according to a previously published procedure [17]. The products were deep red colored. The crystal had an average diameter of approximately 0.4–0.5 μm as observed by using a JEOL JEM 12–20 transmission electron microscope (TEM). The X-ray diffraction pattern (XRD) of the product matched exactly that of α-Fe_2O_3, which was recorded at room temperature by a Philips powder diffractometer using the Cu Kα radiation. It's BET specific surface area determined in a Flow Sorb 2300 apparatus (Micromeritics) was $9.8\,m^2\,g^{-1}$. The product was resuspended in a polypropylene bottle kept in the dark at 277 K. The same batch of α-Fe_2O_3 was used in all of the experiments. All solutions were prepared from analytical grade reagents and doubly distilled water.

The powder of the FA was gained as a gift, which was extracted from the Liaohe River situated in Liaoning province in the northeast of China. The elemental composition of the FA is 45.2% C, 4.1% H, 1.0% N, 49.7% O and <1% ash. The FA suspension was prepared according to the procedures described by Li et al. [18]. The concentrated bulk solution was stored as a stock solution for further use. The FA concentration was measured by a Shimadzu UV-2401 PC instrument at 254 nm (UV_{254}).

γ-HCH (ACS reagent grade, purity ≥ 99.0%) was purchased from National Station of Environmental Monitoring of China without further purification. A primary stock of $4000\,mg\,L^{-1}$ was prepared in acetone and a sub-stock of $5\,mg\,L^{-1}$ ($S_W = 7.8\,mg\,L^{-1}$, 298 K, 1 atm) was gained by dilution of the primary stock solution and was used after 2 days to achieve complete equilibration. Acetone has known to be resistant to degradation in reactions involving hydroxyl radical [15]. The stock solutions were prepared monthly and stored in the dark in the refrigerator.

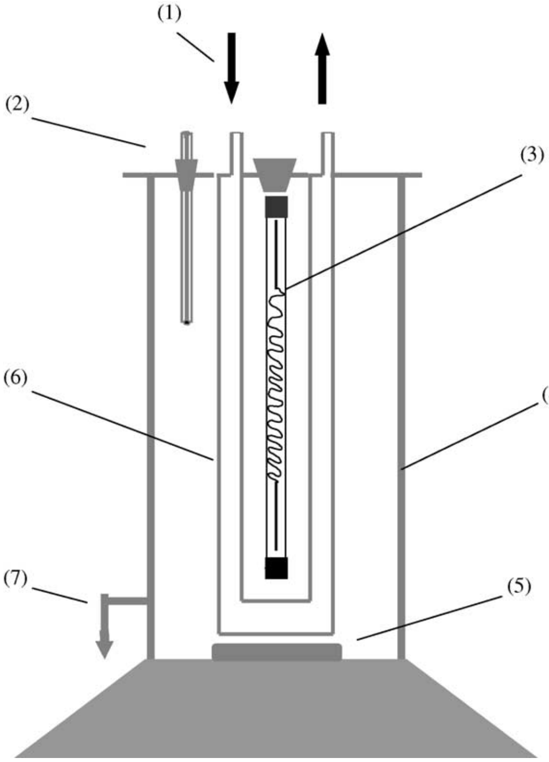

Fig. 1. Photoreactor system for γ-HCH transformation: (1) cooling water; (2) thermometer; (3) high-pressure mercury lamp; (4) glass reactor; (5) stirrer bar; (6) UV lamp cooling; (7) sampling port.

2.2. Experimental setup and procedure

The photochemical experiments were performed in a sealed 300 mL cylindrical reactor. The walls of the water jacket were made of quartz. The outer wall of the reactor was made of the common glass. A 300 W high-pressure mercury lamp was positioned within the inner part of the vessel and cooling water was circulated through a quartz jacket surrounding the lamp. The lamp emitted a wide band of radiation in the full wavelength and did not employ additional filters. The maximum intensity of the lamp occurs at a wavelength of 365 nm. Continuous temperature measurements were made by mean of a thermometer inserted in the reactor. At a distance of 10 cm, the radiant exultance of 300 W yielded $2800\,\mu W\,cm^{-2}$. The photoreactor used in this work was shown in Fig. 1.

The reactor was first filled with the suspension containing α-Fe_2O_3 particles. The required volume of γ-HCH solution was then added, the mixture stirred for an hour in the dark to assure equilibrated state. When a series of experiments was performed in the ternary system (α-Fe_2O_3, the FA and γ-HCH), the mixture solutions of α-Fe_2O_3 and the FA were shaken gently in the dark for 6 h to ensure establishment of equilibrium. The working solutions were acquired when γ-HCH was ultimately added. At given time intervals, samples were collected. All experiments were performed at $T = 293 \pm 1$ K. Studies were typically conducted for 12 h. The solution pH was adjusted by 0.1 M L^{-1} HCl or NaOH.

2.3. Analytical methods

Liguid–liquid extraction with subsequent gas chromatograph (GC) determination was used for the analysis of γ-HCH according to the following procedure: 2 mL of each sample were required. The samples were sequentially added 10 mL mixture of acetone: petroleum ether (1:1; v/v) and immediately sealed to avoid any loss of the analyte, agitated for 20 min and followed by sonicating for 30 min. Following that the samples were transferred to 30 mL separatory funnel. The organic phase was collected, and the aqueous phase was further extracted twice with 5 mL petroleum ether, dried with a small amount of anhydrous Na_2SO_4 and finally analyzed by GC.

A Hewlett-Packard (Hewlett-Packard Co., Avondale, PA) 6890 GC equipped with ^{63}Ni electron capture detector (ECD), a split/splitless injector operated in the splitless mode, a HP-5 column (30 m × 0.32 mm); film thickness 0.25 μm. Operating conditions were as follows: initial column temperature 403 K (1 min), increased at 10 K min^{-1} to 513 K (11 min); injector temperature 523 K; detector temperature 623 K; Carrier gas helium at a flow-rate 1 ml min^{-1}; injection volume 1 μL. Duplicate measurements were made for each sample. A HP chemstation A.05.02 software was used for instrument control and data process.

Intermediate products were identified by a Hewlett Packard HP 5971 mass-selective detector combined with an HP 6890 GC with an HP-5 capillary column. The conditions set for GC–MS were similar to those mentioned above for GC-ECD.

3. Results and discussion

3.1. Photodegradation of γ-HCH by α-Fe_2O_3

3.1.1. Direct photodegradation essay

The influence of UV irradiation was firstly studied. The results were shown in Fig. 2. One can see that γ-HCH could be transformed by UV light alone. 60.7% γ-HCH was degraded after 12 h irradiation. The experiment was also performed in darkness under the same condition; no obvious loss of γ-HCH was observed, suggesting that the loss of γ-HCH due to adsorption onto the walls of the reactor or volatilization can be ignored.

3.1.2. The effect of α-Fe_2O_3 loading on the photodegradation of γ-HCH

The effect of α-Fe_2O_3 loading on the photodegradation of γ-HCH was also observed, as shown in Fig. 3. It was found that the photodegradation of γ-HCH was promoted by α-Fe_2O_3. The pH almost remained constant during the course of the experiment, suggesting that α-Fe_2O_3 have buffer capacity due to the charged surface groups (◊-$FeOH_2^+$; ◊-FeOH; ◊-FeO^-). At the later stage, the loss of γ-HCH became slower. This could be due to the intermediates adsorbed on the iron oxides. These passive effects of intermediates have been reported during the photodegradation of chlorophenol by α-Fe_2O_3 [19]. The intermediates compete with γ-HCH for the active catalytic sites. The control experiments were also carried out. No degradation was observed in the dark.

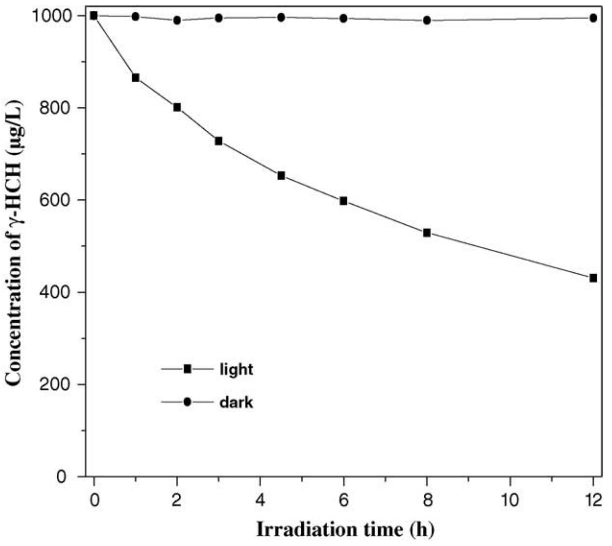

Fig. 2. The direct photodegradation of γ-HCH at pH 4.0 with the illumination of 300 W high-pressure mercury lamp.

α-Fe_2O_3 is expected as an active photocatalyst. Adsorption of a photon with energy greater than the band gap of α-Fe_2O_3 leads to the formation of an electron hole pair (h_{vb}^+/e_{cb}^-). The valence band hole (h_{vb}^+)[E_H = 2.3 eV] is a

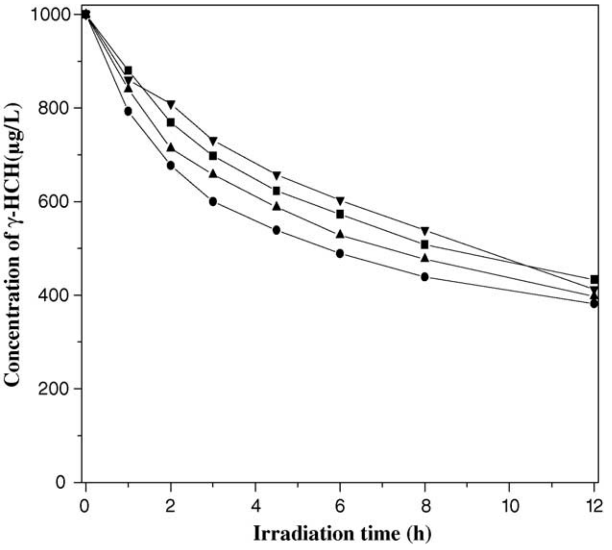

Fig. 3. Photodegradation of γ-HCH under various concentrations of α-Fe_2O_3 induced by UV light, pH 4.0; at the absence of α-Fe_2O_3 (▼); 250 μM L^{-1} (●); 500 μM L^{-1} (■) and 100 μM L^{-1} (▲).

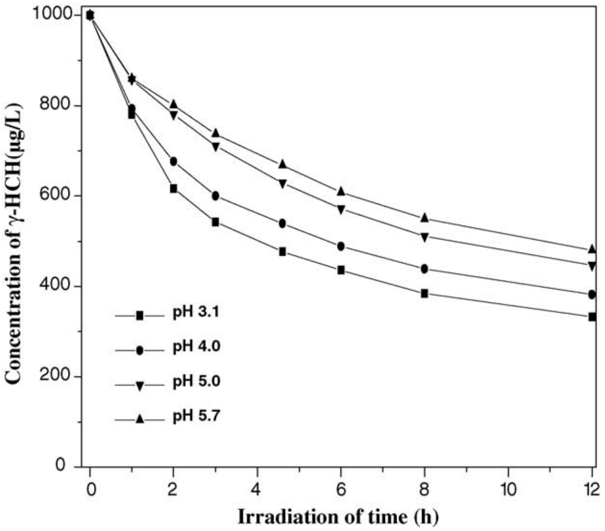

Fig. 4. Photodegradation of γ-HCH in the presence of α-Fe_2O_3 (250 μM L^{-1}) induced by UV light under various pHs.

powerful oxidant while the conduction band electron (e_{cb}^-) [$E_H = 0.0$ eV] has shown to be a relatively poor reductant. Compared to TiO_2, catalytic power of α-Fe_2O_3 is generally poor due to the quick h_{vb}^+/e_{cb}^- recombination, possibly due to a high density of intrinsic mid-bandgap electronic states, internal defect induced trap states, and, to a lesser extent, surface defects [20,21].

It was interesting to find that, instead of promoting effect, the increase of α-Fe_2O_3 loading did not improve the degradation of γ-HCH, as shown in Fig. 3. When α-Fe_2O_3 increased from 250 to 500 μM L^{-1}, after 6 h irradiation the residual fractions of γ-HCH were 51.5 and 54.3%, respectively. Generally speaking, more h_{vb}^+ will be produced when the amount of α-Fe_2O_3 increases. This should lead to a better efficiency of degradation. However, the experiment showed an opposite result. The reason behind this result might be the suspended particles in the solution may scatter incident light, greatly reducing penetration of light when the concentration of α-Fe_2O_3 were increased, result in the slower conversion rate of γ-HCH. Based on this result, the dosage of α-Fe_2O_3 was chosen as 250 μM L^{-1} in subsequent experiments.

3.1.3. The effects of pH on the photodegradation of γ-HCH in the presence of α-Fe_2O_3

To observe the effects of pH on the photodegradation of γ-HCH, four experiments were conducted with the same initial γ-HCH concentration of 1 mg L^{-1}, α-Fe_2O_3 concentration of 250 μM L^{-1} but at different pH (3.0, 3.9, 4.8 and 5.6). The experimental results were shown in Fig. 4. It was evident that the degradation rate of γ-HCH was pH-dependent. The increase pH was companied by the decrease rate. This may be that a fraction of α-Fe_2O_3 transform to amorphous iron oxide at higher pH, resulting in the lower $OH^\bullet$ production rate. On the other hand, α-Fe_2O_3 are more liable to aggregation at higher pH, which lead to the lower photoabsorption efficiency, therefore the slower degradation rate of γ-HCH at a high pH.

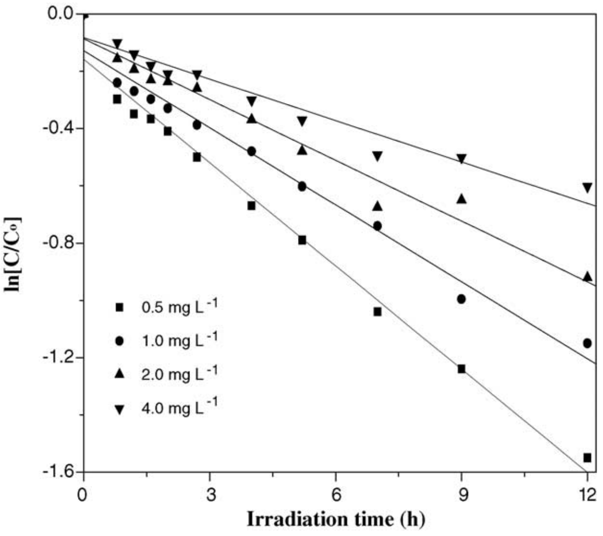

Fig. 5. Plots of In [C/C_0] vs. irradiation time for γ-HCH photodegradation runs carried out in the presence of α-Fe_2O_3 (250 μM L^{-1}). Initial concentration: 0.5, 1.0, 2.0 and 4.0 mg L^{-1}.

3.1.4. The effect of initial γ-HCH concentration on the photodegradation of γ-HCH by α-Fe_2O_3

Four experiments with the same initial pH 4.0, α-Fe_2O_3 of 250 μM L^{-1}, but different initial γ-HCH concentrations were conducted in the presence of UV irradiation.

γ-HCH photodegradation by α-Fe_2O_3 was found to occur according to the Langmuir–Hinshelwood rate law, i.e.:

$$r = -\frac{dC}{dt} = \frac{k_r K_a C}{1 + K_a C} \quad (1)$$

The equation can be simplified to a pseudo-first-order equation:

$$\ln \frac{C_0}{C} = k_\gamma K_a t = k' t \quad (2)$$

Indeed, straight lines were obtained by plotting In [C/C_0] versus time (Fig. 5) and the apparent first-order rate constants k' (Table 1), calculated from the slope of these plots, were inversely proportional to C_0, the initial γ-HCH concentration. Therefore, the experimental result indicated that photodegradation of γ-HCH by α-Fe_2O_3 was fitted for a pseudo-first-order kinetics. The degradation rate increased with increasing γ-HCH concentration, but the apparent kinetic constant k' decreased with increasing γ-HCH concentration.

Table 1
Photodegradation kinetics data of γ-HCH by α-Fe_2O_3

C_0 (mg L^{-1})	k (h^{-1})	R^2
0.5	0.0855	0.9835
1.0	0.0820	0.9768
2.0	0.0662	0.9674
4.0	0.0588	0.9451

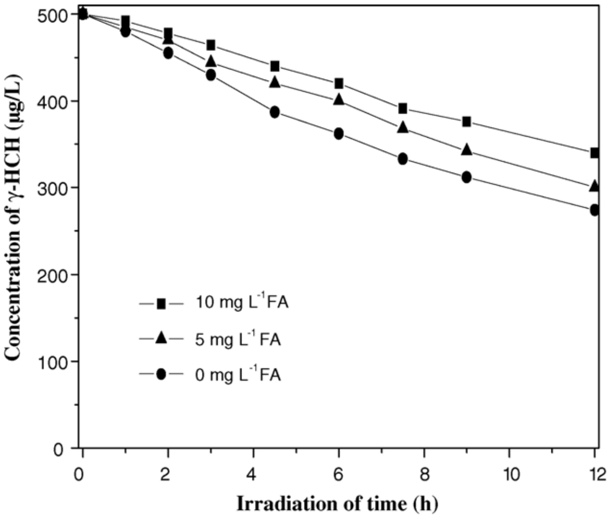

Fig. 6. Photodegradation of γ-HCH in the presence of various concentrations of FA induced by UV light, pH 4.0.

3.2. The effect of the FA in the photodegradation of γ-HCH

3.2.1. The effect of the FA in the photodegradation of γ-HCH

The experiments were carried out with the same initial γ-HCH concentration of 0.5 mg L^{-1}, but at two FA concentrations (5 and 10 mg L^{-1}) at pH 4.0. The controlled experiment was performed at the same condition but in the absence of the FA. The degradation curves (Fig. 6) demonstrated that the photodegradation of γ-HCH was slower in the presence of the FA. After 6 h UV light exposure, the loss of γ-HCH was 27.6, 20.0, and 16.0% for solutions at the absence of the FA, 5 and 10 mg L^{-1} FA, respectively. This demonstrated that the FA slowed the transformation rate of γ-HCH.

The decrease rate could be due either to the FA competing with γ-HCH for the available photons or to binding between humic molecules and γ-HCH. It has been reported that HS can react photochemically [22,23]. On the other hand, when γ-HCH and the FA coexist in solution, a certain fraction of the pesticide is possibly bound to the FA. We speculated that the binding between α-Fe_2O_3 and the humic molecular occur predominantly because the non-polar γ-HCH molecules were excluded by polar H_2O molecules, thus preferring to binding to the FA (Eqs. (3) and (4)):

$$\mathrm{L} + \mathrm{FA} \overset{k_b}{\longleftrightarrow} \mathrm{L} - \mathrm{FA} \tag{3}$$

$$k_b = \frac{[\mathrm{L} - \mathrm{FA}]}{[\mathrm{L}][\mathrm{FA}]} \tag{4}$$

On the basis of a large number of other results from previous studies of photosensitized reactions in solution [10,22–25], the absorption of light by HSs can lead to rapid photosensitized reactions of many pollutants via energy transfer from

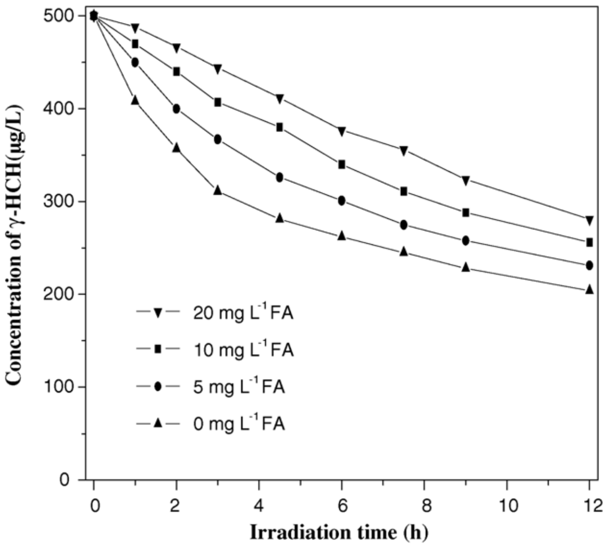

Fig. 7. Photodegradation of γ-HCH by α-Fe_2O_3 (250 μM L^{-1}) in the presence of various concentrations of the FA induced by UV light, pH 4.0.

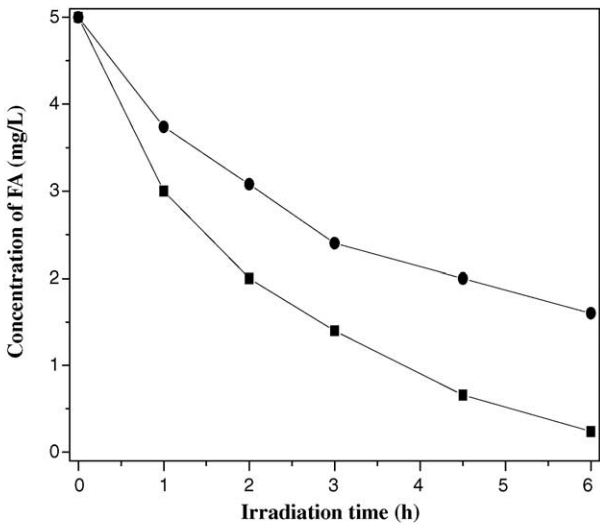

Fig. 8. Photodegradation of FA by α-Fe_2O_3 in the presence of 0.5 mg L^{-1} γ-HCH at pH 4.0 exposed to UV light. In the absence of α-Fe_2O_3 (●); 250 μM L^{-1} α-Fe_2O_3 (■).

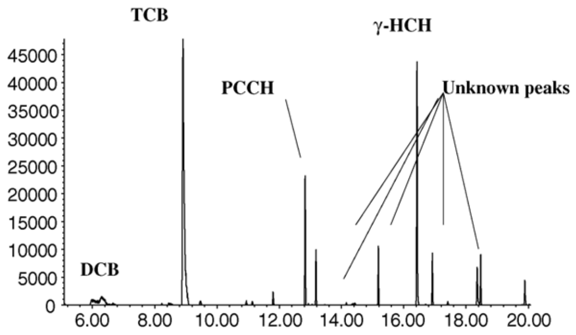

Fig. 9. GC–MS chromatogram; photodegradation of γ-HCH (1 mg L^{-1}) by α-Fe_2O_3 after 6 h.

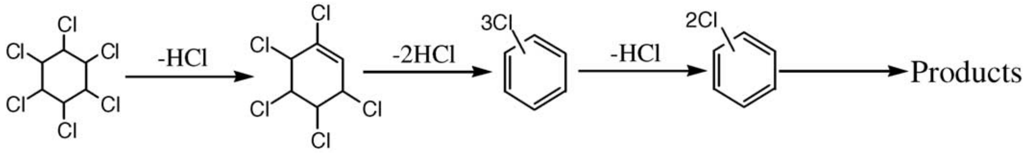

Fig. 10. Possible degradation pathways of γ-HCH.

molecules in their triplet states (Eqs. (5) and (6)):

$$\mathrm{HS} \xrightarrow{\text{light}} {}^1\mathrm{HS}^* \rightarrow {}^3\mathrm{HS}^* \qquad (5)$$

$$^3\mathrm{HS}^* + \mathrm{P} \xrightarrow{k_\mathrm{p}} \mathrm{HS} + \mathrm{P}' \qquad (6)$$

$$^3\mathrm{HS}^* \xrightarrow{k_\mathrm{d}} \mathrm{HS} + \text{heat} \qquad (7)$$

$$^3\mathrm{HS}^* + \mathrm{Q} \xrightarrow{k_\mathrm{q}} \mathrm{HS} \qquad (8)$$

$$\mathrm{L}-\mathrm{HS} \xrightarrow{\text{light}} \mathrm{L}^*-\mathrm{HS} \rightarrow \mathrm{L}-\mathrm{HS}^* \qquad (9)$$

However, Zepp et al. [25] has found, only when the pollutants with triplet state energies are less than 250 kJ mol^{-1} these photoreactions can be sensitized by HS. Furthermore, on these systems ^{3}HS* will be deactivated by a variety of pathways, such as decay to ground state (Eq. (7)) or other interaction that quenches ^{3}HS* (Eq. (8)). In our study, the sensitization effect of the FA on the γ-HCH photolysis was not found. The photodegradation of γ-HCH was clearly retarded by the FA. It may be the cause that γ-HCH transfers the energy adsorbed by itself to the surrounding humic molecules by mean of the binding formed between the FA and γ-HCH molecules (Eq. (9)).

3.2.2. The effect of the FA in the photodegradation of γ-HCH in the presence of α-Fe_2O_3

Experiments were also conducted with 0.5 mg L^{-1} initial γ-HCH and 250 μM L^{-1} α-Fe_2O_3 in the presence of various FA concentrations (0, 5, 10 mg L^{-1}) at pH 4.0. The result was shown in Fig. 7. In all cases the FA slowed the transformation rate of γ-HCH. For example, after 3 h irradiation the loss of γ-HCH was 19.6, 25 and 33.8% for solutions with 10, 5 mg L^{-1} FA and at the absence of the FA, respectively. It was apparent that increasing FA concentration decreased the slope of the rate plots, indicating a decreasing reaction rate.

When the FA was introduced into the binary system (γ-HCH/α-Fe_2O_3), the circumstance may be different. In the same solution, it was found that the FA was rapidly photodegraded by α-Fe_2O_3, which was shown in Fig. 8. Therefore, it could be speculated the humic molecular adsorbed onto the surface of α-Fe_2O_3, act as scavengers of valence band holes ($h_{\mathrm{vb}}{}^+$) due to its electron-rich nature, thus slowing down the degradation of γ-HCH occurred on the semiconductor surface. Besides, when a preequilibrium formed between the FA and α-Fe_2O_3, it is difficult for γ-HCH molecular to contact $h_{\mathrm{vb}}{}^+$ due to the obstructiveness of the layer of the FA molecular, which may be the other reason that the FA play a passive role on photodegradation of γ-HCH by α-Fe_2O_3.

4. Identified intermediate and proposed reaction pathways

Intermediate products were identified by GC–MS techniques. The results were shown in Fig. 9. Pentachlorocyclohexen (PCCH), trichlorobenzene (TCBs), and dichlorobenzene (DCBs) were identified after 6 h irradiation in the presence of α-Fe_2O_3.

Fig. 10 showed a possible pathway of γ-HCH photodegradation reaction proposed for α-Fe_2O_3 -containing system based on the identified intermediate. The first step of photodegradation is likely the formation of PCCH via anti-periplanar dehydrohalogenation, a commonly believed base degradation mechanism [14], through a bimolecular elimination reaction in which abstraction of the hydrogen on the carbon occurs simultaneously with cleavage of the C−X bond, forming a carbon–carbon bond. PCCH may be further dehydrochlorinated via direct formation of TCBs via simultaneous eliminations of two chlorine and two hydrogen atoms from PCCHs. TCBs are further transformed to DCBs by eliminations of one chlorine.

Intermediate products were identified in a photocatalytically treated solution containing high concentration of γ-HCH [15]. Several specified or unspecified isomers were found as the degradation products, including chlorocyclohexanes, chlorocyclohexenes, chlorobenzenes, chlorophenols, chloropropanes and chloropropanones, and the pentachlorocyclohexanone isomer. The nature of by-products showed that chlorine and hydrogen atoms were not only abstracted from the CHCl groups constituting γ-HCH but also added to them because heptachlorocyclohexane was detected. In the solution containing γ-HCH, which was photocatalytically treated by TiO_2, α-HCH, an HCH isomer, were also identified [15].

5. Conclusions

It is clear that both α-Fe_2O_3 and UV light have an accelerating effect on the degradation of γ-HCH, and γ-HCH transformed by α-Fe_2O_3 photochemically follows a pseudo-first-order reaction. However, the degradation efficiency of γ-HCH by α-Fe_2O_3 was lower compared to TiO_2 on the basis of the former study. The degradation rate of γ-HCH by α-Fe_2O_3 was pH-dependent, an increase in pH was accompanied with a decrease in the rate of γ-HCH. In any case, FA slowed the transformation rate of γ-HCH. This could be that FA catch the holes generated on the surface of α-Fe_2O_3.

FA bound with γ-HCH molecular in the suspension, could be the other cause. A dehydrohalogenation pathway from γ-HCH to PCCH followed to TCBs and DCBs is proposed for the photodegradation of γ-HCH in the presence of α-Fe_2O_3.

For natural environments, HS can be expected to diminish the strength of light-induced degradation of γ-HCH to some extent, occurring at the surface of mineral oxides with semiconducting properties in natural water. Because of the abundance of HSs in the natural environment, the observed retardation effects of HSs possess a major engineering concern if photolysis is applied in remediation of contaminated natural waters.

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