

Photodegradation Study of 1, 3, 5-Trichlorobenzene Using Pt(IV)/AMM-Ti Photocatalyst in Humic Acid (HA) Solution

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Pt(IV)/AMM-Ti 광촉매를 이용한 휴믹산에서의 1, 3, 5-Trichlorobenzene의 광분해반응의 연구

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요 약

1,3,5-TCB의 광분해를 목적으로 Pt(IV)/AMM-Ti 광촉매의 산화반응을 이용하여 조사시간, 농도, pH의 변수에 대한 효과 및 광분해물질의 성분분석과 휴믹산의 1,3,5-TCB의 분해에 미치는 영향을 연구하였다.

Key words : Pt(IV)/AMM-Ti, photodegradation, 1,3,5-TCB, humic acid (HA)

INTRODUCTION

TCBs are well known to possess toxic and harmful effects when they are exposed to aquatic species in the ecosystem. Of the TCB isomers, 1, 3, 5-TCB is the most recalcitrant one to degrade with bacteria in aqueous systems.¹⁾ Oxidative dechlorination reactions have occurred quickly with 1,2,3- and 1,2,4-TCB to produce dichlorobenzenes, but very slowly with 1,3,5-TCB.²⁾

Because of its high photocatalytic activity and photostability, TiO₂ has been widely used for the application of water and wastewater treatment.³⁾ Although the TiO₂ in colloidal suspensions has been proven as an excellent catalyst for degradation of pollutants, various doping methods were employed for enhancement of photooxidation/photoreduction,

where an efficient charge separation is attained upon excitation with UV light.⁴⁾⁻⁸⁾ However the TiO₂ emulsion has a limitation on the treatment of waste stream because of recovery of the particles in emulsion. The other disadvantage of the titania or doped-titania suspension for onsite application was a light source, which is to employ UV light to degrade pollutants, and some of photocatalysts are known to be corrosive in solutions. The amorphous titania modified with platinum (IV) chloride (Pt(IV)/AMM-Ti) photocatalyst has been reported to be photoreactive in visible region.⁹⁾

Humic acid is widely known to photogenerate electrons and free radicals and quinones which seem to accelerate photodechlorination/photooxidation of chlorinated aromatic compounds in UV or visible region.¹⁰⁾ Even though the addition of humic acid can

cause a decrease in the TiO_2 -catalytic oxidation of 2-chlorobiphenyl,¹¹⁾ electrons transfer from humic acid may incorporate Pt (IV)/AMM-Ti to get more efficient charge separation of the bandgaps so that reduction/oxidation reactions may occur more faster than without humic acid. The degradation of humic acid,¹²⁾ or fulvic acid¹³⁾ in water by means of photocatalytic method has been studied. The positive energy transfer mechanism in HA solution has been investigated with monochlorobenzene or PCBs directly or indirectly.¹⁰⁾

In this paper, we described the effectiveness to degrade 1, 3, 5-TCB using Pt (IV)/AMM-Ti photocatalyst in humic acid solution that is a possible treatment method of 1, 3, 5-TCB. The degradation kinetics and possible photocatalytic mechanisms were investigated.

EXPERIMENTAL

1. Materials and procedure

1, 3, 5-TCB and all the other agents were of analytical grade and used without further purification. Titanium isopropoxide was purchased from Aldrich. The hybride titania (Pt(IV)/AMM-Ti) was prepared by a sol-gel method. The catalyst containing 1.1% (W/W) of Pt (IV)/AMM-Ti was prepared as follows: 12 mL of $\text{Ti}(\text{OC}_3\text{H}_7)_4$ (0.04 M) was dissolved in 50 mL of ethanol and stirred for 30 min, followed by slow addition of 0.1 mL of 8 M HCl. After that, 0.1 mL of conc. HCl was added every 10 min for two times. Thereafter, 0.105 g (1.87×10^{-4} mol) of $\text{Na}_2\text{PtCl}_6\text{H}_2\text{O}$ dissolved in 10 mL of ethanol was added slowly. The resulted clear yellow solution was then stirred at room temperature for 1 day. For drying, the gel was kept uncovered for another 10 days in a hood. The solidified gel was heated to 65°C at the heating rate of 0.1°C/min, kept at this temperature for 100 min, and then heated at the same rate to 250°C. After sustaining for 300 min at 250°C, it was allowed to cool to room temperature. Materials were ground in a ball mill to provide small particles for suspen-

sion in water. Both 2 g of the ground photocatalyst and 0.1 g of humic acid were dissolved by stirring in 1 L distilled water of two 2 L flask for 24 hrs to enhance complexation, then air was saturated into the reaction solution before exposure. All experiments were performed at an initial pH of 7.0.

1) Kinetic study

A merry-go-round photoreactor set up with 8 (10-watt) black lamps ($\lambda_{\text{max}} = 350$ nm) was used in this study. The samples in test tubes were taken at different time intervals for analysis by GC to determine the remaining concentration of the parent compound. After illumination, samples were taken intermediately for analysis. The HA solution was made in 2 L flask where 5 gram of HA was added and stirred for 24 hrs. Then, the solution was exposes under atm without stirring to precipitate the HA. Each 1 mL of the upper solution was taken into the test tubes for the experiment (kinetic and product studies). The experimental data were obtained from a run at pH 7 under air.

2) Photoproduct study

Large-scale exposure solutions with 5 ppm 1, 3, 5-TCB were prepared to isolate sufficient quantities of photoproducts for structural characterization. The samples (1 L) were irradiated in 2 L Pyrex round-bottom flask in the photoreactor except one sample which was covered with aluminum foil. The lid of reactor was widely opened to get maximum visible light from outside. The exposed samples were extracted with hexane for the GC/MS analysis.

ANALYTICAL METHOD

The GC/MS analyses were performed with a Finnigan Ion Trap Mass Spectrometer coupled to a Varian 3000 GC equipped with DB-5 fused silica capillary column (a 30 m \times 0.25 mm i.d.). The GC temperature program used was an initial temperature of 40°C, increased to 60°C/min and held for 2 min at 180°C. The second temperature ramp was increased at 4°C/min to 180°C and third was increased at the rate of

10°C/min to 270°C and held until completion.

RESULTS AND DISCUSSION

1. Kinetic study

In a separate experiment in which TCB alone was degraded, no dechlorinated byproduct was produced from the photocatalytic degradation of TCB, assuming that dechlorination may occur by another route as well.

It is seen from the kinetic curves depicted in the Fig. 1 that the rates of photocatalytic degradation of 1,3,5-TCB decreases slightly in the presence of humic acid for 4 days and then increased sharply from 4 day. It is clear that the photooxidation efficiency decreased with exposure duration after 4 days in the presence of humic acid, suggesting the absorption efficiency is inhibited by humic acid (Fig. 1). In terms of photochemical mechanisms, the observed decrease on the kinetic rate of 1,3,5-TCB degradation can be attributed to the fact that, firstly, energy transfer mechanism *via* humic acid does not occur in the solution; secondly, the light-absorption efficiency

is inhibited by humic acid for 4 days; thirdly, the catalyst produces efficient electrons to participate in the photolytic oxidation/reduction process; lastly, photodegraded humic acid also photoproduce electrons to react with oxygen radical species after 4 days.

When a small amount of a strong acid (HCl) or base (NaOH) is added into the initial suspension, the photodegradation efficiency increases or decreases in a (Table 1). The results did not show any difference in photolysis rate in different pH.

2. Photoproduct study

The oxidation process was performed in a small-

Table 1. Photolysis rate in HA for 3 days in different pH

pH	Photolysis rate of 1,3,5-TCB (%)
3.5	46
5.6	53
6.7	52
7.0	46
8.2	48
9.1	47
10.0	45

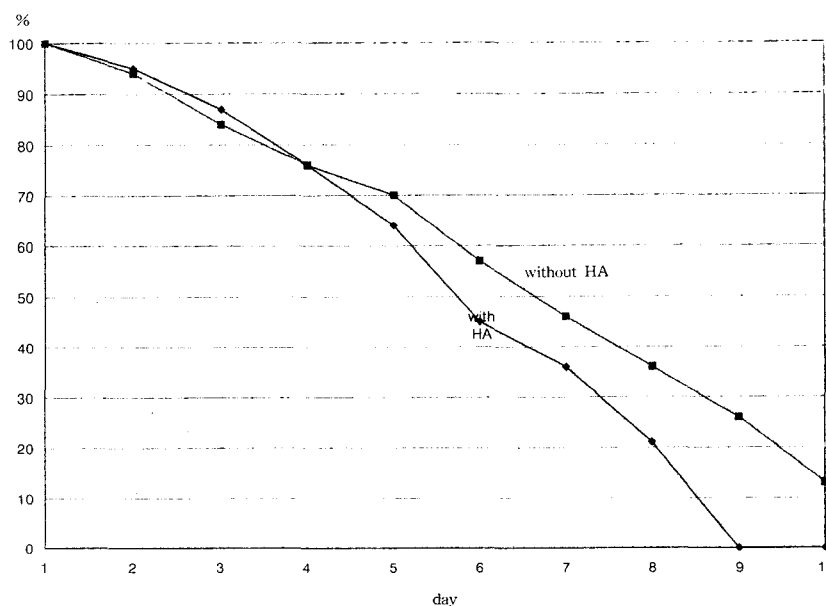


Fig. 1. Kinetic plot for the photolysis of 1,3,5-TCB in the presence of HA and Pt(IV)/AMM-Ti for 10 days.

scale batch reactor. The results of the batch reactor tests pointed out that two different degradation mechanisms took place in a batch reactor. The mechanisms of photocatalytic degradation of organic pollutants have been well known. The photoproduct study showed the main product, as a 2,4,6-trichlorophenol for 4 days, then the product was transformed to dichlorophenols. Two different mechanisms are involved in the homogeneous photochemical process:

the photochemical oxidation promoted by hydroxyl radicals, superoxide and oxygen and the photodechlorination due to the direct excitation of the reactants by UV light. The complete degradation can be achieved through the heterogeneous photocatalytic reaction for 10 days where the effect of HA was very prominent (Fig. 2). Another experiment in the presence of Pt (IV)/AMM-Ti showed that photoreductive dechlorination occurred to produce 1,3-di-

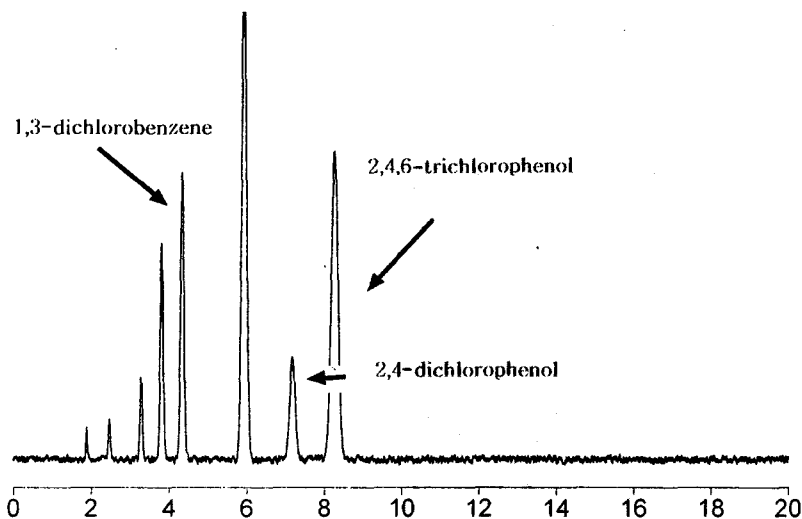


Fig. 2. GC chromatogram of photoproducts of 1,3,5-TCB after exposure in the presence of catalyst and HA for 8 days.

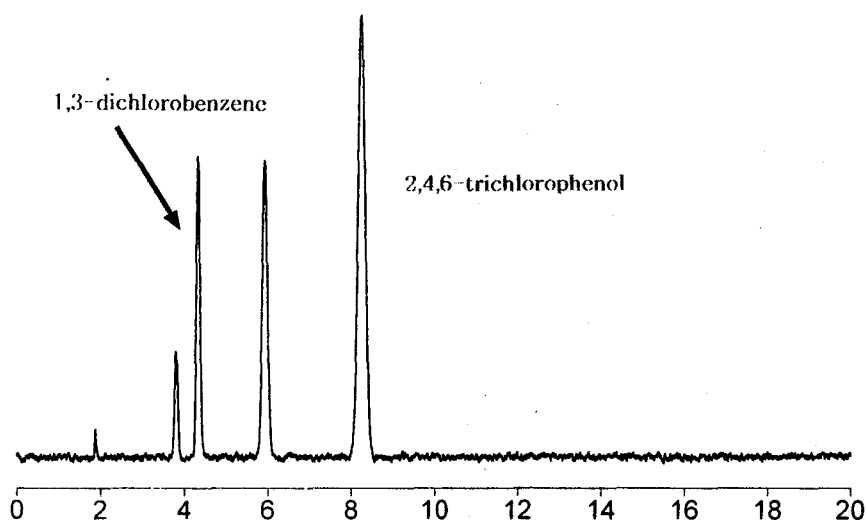


Fig. 3. GC chromatogram of photoproducts of 1,3,5-TCB after exposure in the presence of catalyst only for 8 days.

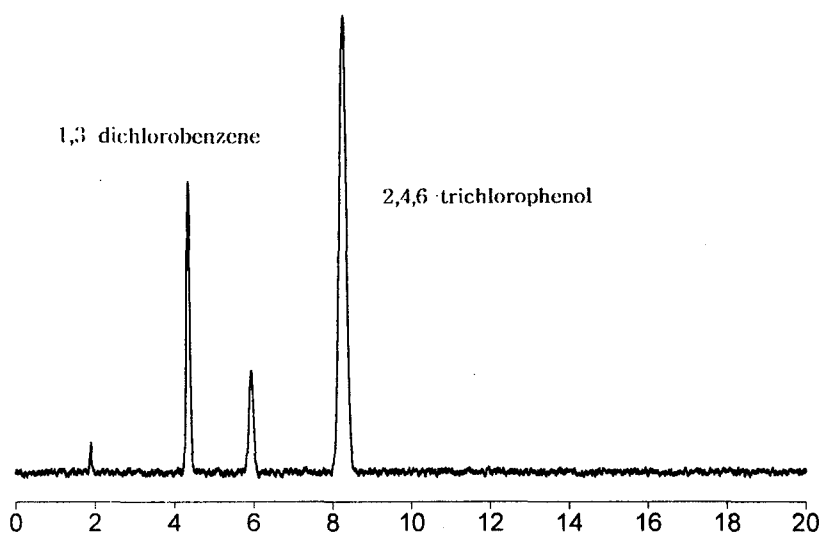


Fig. 4. GC chromatogram of photoproducts of 1,3,5-TCB after exposure in the presence of HA only for 8 days.

chlorobenzene and 2,4,6-trichlorophenol (Fig. 3). Photolysis of 1,3,5-TCB with a 360 nm light in the presence of only humic acid also produced dechlorinated photoproducts such as 1,3-dichlorobenzene and 2,4,6-trichlorophenol (Fig. 4).

The results confirmed that observed decrease on the kinetic rate of 1,3,5-TCB degradation for 4 days and a major trichlorophenol product can be attributed to the fact that energy transfer mechanism does not affect the photolysis rate in either studies. But it seems to undergo, *via* efficient electrons emitted from the catalyst, to participate in the photolytic oxidation/reduction process with electrons and oxygen radical species from photodegrading HA.

CONCLUSIONS

The present study showed that 5 ppm of the 1,3,5-TCB can be completely photodegraded within 10 days. The effect of the humic acid demonstrated an increasing photolytic effect on the compounds, implying that the mechanism seems to occur via hydroxylation not energy transfer which will initiate a dechlorination reaction. Comparison of this reaction to photolysis of 1,3,5-TCB in the absence of HA

leads to the conclusion that the reactive pathway for the degradation of 1,3,5-TCB is due to reaction with singlet oxygen produced by irradiation of the humic material. The control experiments clearly demonstrate that the photodegradation of 1,3,5-TCB is clearly initiated not by the direct reductive dechlorination but by the indirect hydroxylation.

ABSTRACT

The photocatalytic oxidation of the model compound, 1,3,5-trichlorobenzene (1,3,5-TCB) has been investigated employing photolysis. The effects of parameters such as illumination time, initial concentration, pH and HA were investigated. Pt (IV)/AMM-Ti particles used as a photocatalyst showed a time-dependent enhancement of the photooxidation/reduction activity in the presence of HA.

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