

Full Length Research Paper

Kinetics of the photocatalytic degradation of chlorendic acid (flame retardant) in aqueous TiO₂ suspension

Boisa N.* and Obunwo C. C.

Department of Chemistry, Rivers State University of Science and Technology, Port Harcourt, Nigeria.

Kinetics of the Photocatalytic degradation of chlorendic acid [1, 4, 5, 6, 7, 7-hexachlorobicyclo-(2, 2, 1)-hept-5-ene-2, 3-dicarboxylic acid], a flame retardant found in the environment, has been investigated in aqueous heterogeneous solutions using TiO₂ (Degussa P-25) powder in the presence of artificial ultraviolet radiation and oxygen. High-performance liquid chromatography (HPLC) with detector set at 221 nm was used to monitor the concentration of chlorendic acid during the degradation. The degradation kinetics followed a Langmuir-Hinshelwood type equation. The apparent photocatalytic rate constant k , was calculated as $12.0 \pm 1.38 \text{ mg L}^{-1} \text{ min}^{-1}$. The influence temperature and catalyst loading were studied. Results showed that initial degradation rates increased with reaction temperature. The optimal TiO₂ concentration for the photocatalytic process was determined as of 2 g/L. Kinetic data on the degradation of persistent organic pollutants will assist in the design of efficient protocols for their removal from the environment.

Key words: Chlorendic acid, TiO₂, High-performance liquid chromatography (HPLC) and degradation.

INTRODUCTION

Chlorendic acid (Figure 1) is used mainly as a flame-retardant monomer in polyester resins, epoxy resins and polyurethane foams (<http://ntp.niehs.nih.gov/ntp/roc/elevanth/profiles/s033chl.o.pdf> seen, 2016). It also serves as a hardening agent for epoxy resins used in printed circuit boards (<http://ntp.niehs.nih.gov/ntp/roc/elevanth/profiles/s033chl.o.pdf> seen, 2016). In 1981 chlorendic acid was listed as a priority chemical and thus recommended for acute and chronic toxicity tests to aquatic invertebrates, macrophytes, algae, and fish (Federal Register, 1982). The release of chlorendic acid to the environment may

occur during preparation of flame retardant polymers, and subsequent hydrolysis of chlorendic anhydride (Federal Register, 1982; Segev et al., 2009). The solubility of chlorendic acid in water is 0.35 g/100 g at 22.8°C (Honda, 2004) and based on this, in the environment favours the aqueous compartments (Federal Register, 1982). Its degradation in the environment is slow (Federal Register, 1982). The desire to find faster methods of degrading known environmental pollutants has led researchers to try catalyst, including photocatalyst like titanium dioxide (TiO₂). Photocatalytic degradation with TiO₂ is an evolving method for the removal of organic

*Corresponding author. E-mail: boisa.ndokiari@ust.edu.ng.

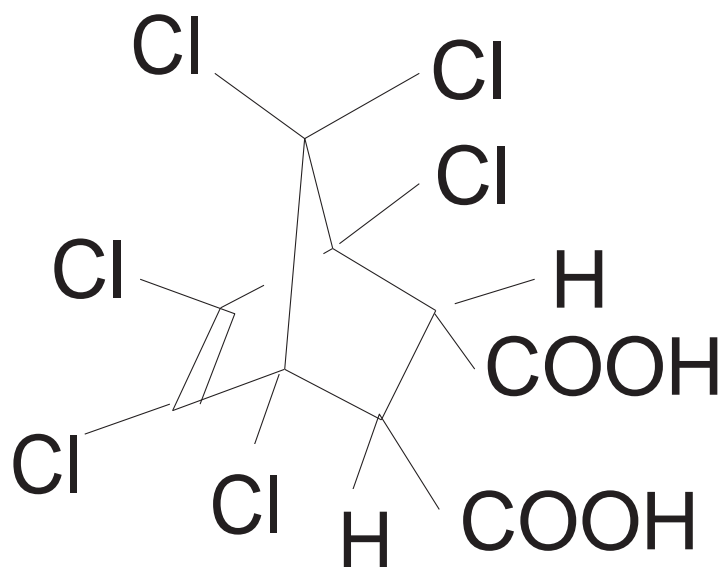


Figure 1. Molecular structures of chlorendic acid.

pollutants from water (Honda, 2004). The investigation of the kinetics of degradation of chlorendic acid with TiO_2 is the focus of this study.

Chlorendic acid bears the hexachloronorborene unit in its molecular structure. The hexachloronorborene unit is degraded only slowly after application in the environment. The hexachloronorborene structure renders it inert to chemical and biological degradation. The inertness can be explained by steric and inductive effects due to the chloride atoms (Schulte-Hostede et al., 1978). They bioaccumulate and biomagnify in animals that are higher in the food chain (Cochrane and Fobres, 1974). In a feed study conducted for a period of 24 months, results indicated clear evidence that chlorendic acid is carcinogenic in male and female rats and male mice (<http://www.inchem.org/document/iarc/vol48/48-01.html> seen, 2016). It has been suggested to be a human carcinogen

(<http://www.inchem.org/document/iarc/vol48/48-01.html> seen, 2016; <http://www.inchem.org/document/ehc/ehc/ehc185.htm#SubSectionnumber:1.16> seen, 2016). Several techniques have been attempted for the removal of chlorendic acid from water. The methods included, enhancement of the SBRs process with activated carbon (Honda, 2004; He et al., 2009), enhancement with different solar conditions (Rashed and El-Amin, 2007) and ozonation (Stowell and Jensen, 1991). Of the methods listed only ozonation achieved close to 100% degradation but this method requires the use of environmentally toxic organic solvents. The heterogeneous catalysis with TiO_2 has been a promising method for the removal of organic pollutants from water. Titanium dioxide (TiO_2) is metal oxide that undergoes photo-excitation in the presence of

light; displaying a relatively high efficiency when applied as a photocatalyst. One of the unique features exhibited by TiO_2 is that it absorbs irradiation that falls within the near UV- visible region.

The titanium dioxide used for this experiment is the Degussa P-25; a binary mixture of the rutile (20%) and the anatase (80%) form. The Degussa P-25 has a specific BET area of $50 \text{ m}^2\text{g}^{-1}$ and a mean particle size of 21 nm. At the molecular level the photocatalysis process involves; diffusion towards the catalyst surface, adsorption, surface reactions, product desorption and diffusion away from the catalyst surface. The aim of this study is to investigate the kinetics of the photodegradation of chlorendic acid using titanium dioxide (TiO_2) as the photocatalyst.

Experimental

Titanium dioxide (TiO_2) photocatalyst was used as obtained from the laboratory. Chlorendic acid (99% purity) was purchased from Sigma-Aldrich Logistik GmbH, Germany, and used as received. 6.0 M nitric acid solution, 0.1M potassium thiocyanate solution and 0.5% tartrazine indicator were freshly prepared from analytical grade chemicals available in the Laboratory. 0.1 M silver nitrate solution and HCl solutions were prepared from available stock solutions.

A laboratory built photoreactor (Boisa, 2013) was employed for this study. The UV-Visible absorption spectra were recorded using UV Evolution 300 (Thermo Electron Corporation) spectrophotometer. The high-performance liquid chromatography-diode array detector (HPLC-DAD) with a Varian 9050 HPLC system interfaced with a Jasco PU-980 pump and a SP 4270 integrator was

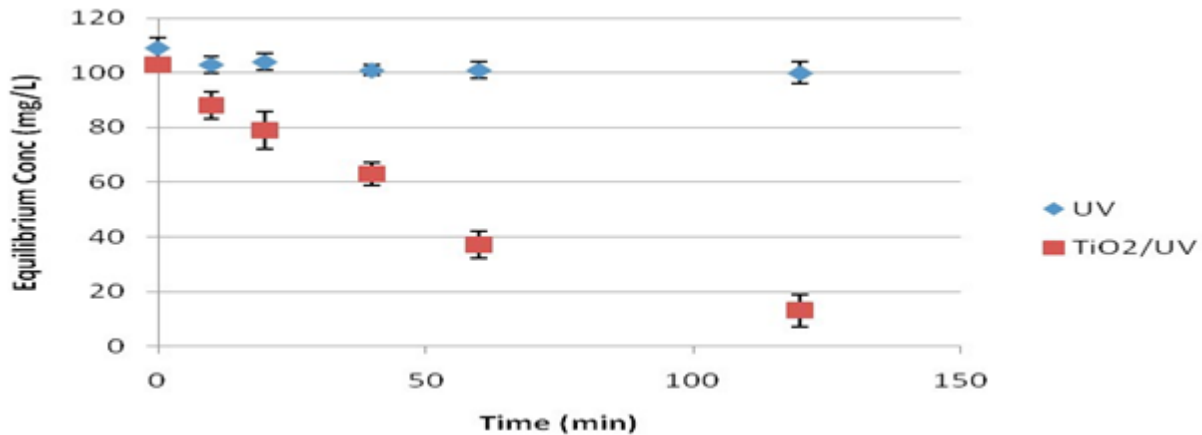


Figure 2. Photolysis and photocatalysis of chlorendic acid at 25°C.

used to analyze chlorendic acid. A Centaur MSE centrifuge instrument was used to precipitate the titanium dioxide in aliquots collected for analyses. A Jenway 3010 pH meter with a 662-1759 international probe was used for the measurement of aliquots extracted during photodegradation reaction.

All chlorendic acid solutions used during this were systematically obtained from a 1000 mg/L stock solution. A 100 mg/L solution of chlorendic acid was scanned with the UV-visible spectrophotometer to obtain the absorption spectrum. Nine working solutions of concentrations ranging from 10 to 500 mg/L were prepared for calibration plot with the HPLC instrument set at 221 nm. For the Kinetic study duplicate aqueous suspensions of chlorendic acid (200 mL, at fixed concentrations) and TiO₂ (1.0 g) were placed in 400 mL Pyrex beaker and left in the dark for 20 minutes to permit the adsorption/desorption equilibrium to be reached, then subsequently irradiated with the UV lamp, under oxygen-equilibrated conditions in the photoreactor. To investigate the influence of UV radiation, the degradation process was also conducted with the UV lamps switched on but without TiO₂. Also the experiment was conducted using varying concentrations of the catalyst and at different temperatures. At designated times samples were extracted from the reacting systems with pipette, centrifuged, filtered, and analysed quantitatively with the HPLC instrument. Artificial sea water of 600 mg / L chlorendic acid was prepared and subjected to photodegradation at optimal conditions identified during this study.

RESULTS AND DISCUSSION

The degradation of chlorendic acid with UV radiation alone and with UV radiation and TiO₂ photocatalyst were investigated. The equilibrium concentrations between 0-

120 min suggested slow degradation with UV radiation when compared with UV radiation and TiO₂ (Figure 2). Based on these data it can be suggested the photocatalyst facilitates the degradation of chlorendic acid in water. To assess the efficiency of TiO₂ as a photocatalyst varying initial concentrations of the acid were subjected to photodegradation. The results suggest that the photocatalyst was effective in degrading the acid at concentrations between 105-254 mg/L (Figure 3). For the studied concentrations after 60 min of TiO₂ aided photodegradation about 50% of the initial equilibrium concentrations were degraded (Figure 2).

Variation in the initial rate of decomposition of chlorendic acid as a function of catalyst loading was investigated. It can be seen that the initial rate of degradation increases proportionally to the concentration of the catalyst until it gets to ~ 2 g / L, then it starts decreasing as the concentration of the catalyst is increased (Figure 4). Above the value of 2 g / L the initial rate is affected negatively by increasing TiO₂ loading. The decrease in reaction rate occurred because the rate became dependent on the screening effect of the excess particles. The excess particles mask part of the photosensitized surfaces, this happens when the solution layer thickness exceeds the optical penetration length at the applied illumination (Carp et al., 2004). The optimal concentration of TiO₂ (2 g/L) obtained for chlorendic acid during this study fall within the range (0.15 to 8 g/L) reported (Honda, 2004; Cochrane and Fobres, 1974) for several slurry photoreactors employing TiO₂. The rate of degradation of the chlorendic acid increases proportionally with temperature within temperature range (20-40°C) selected for this study. This suggests that the photodegradation process is enhanced by increased temperature (Figure 5). The effect of temperature on degradation may be dominated by the rapid desorption of substrates and intermediates from the surface of the TiO₂ catalyst. The dependence of desorption of

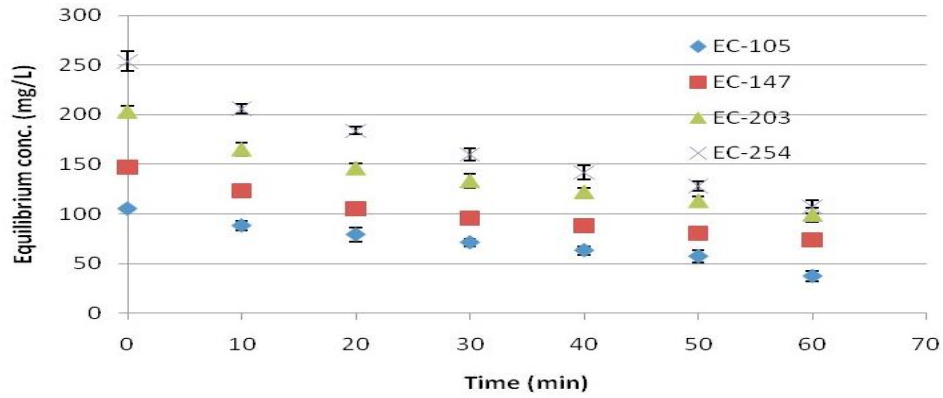


Figure 3. Chlorendic acid photocatalytic degradation trends for varying equilibrium concentrations.

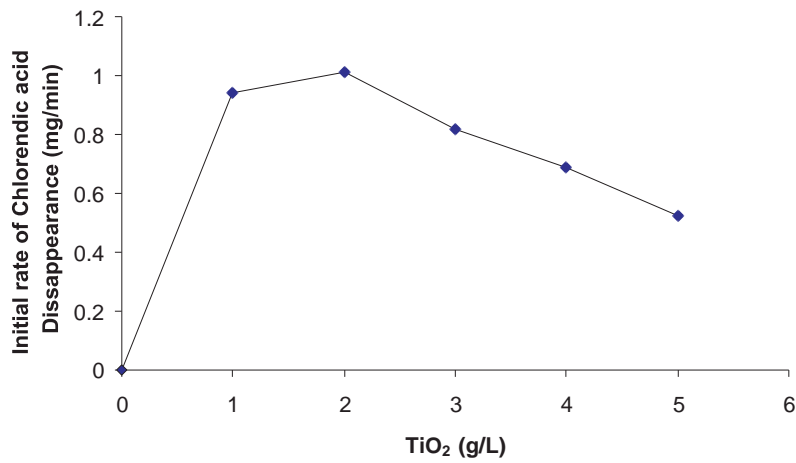


Figure 4. Variation of the initial rate of chlorendic acid disappearance as a function of concentration of catalyst.

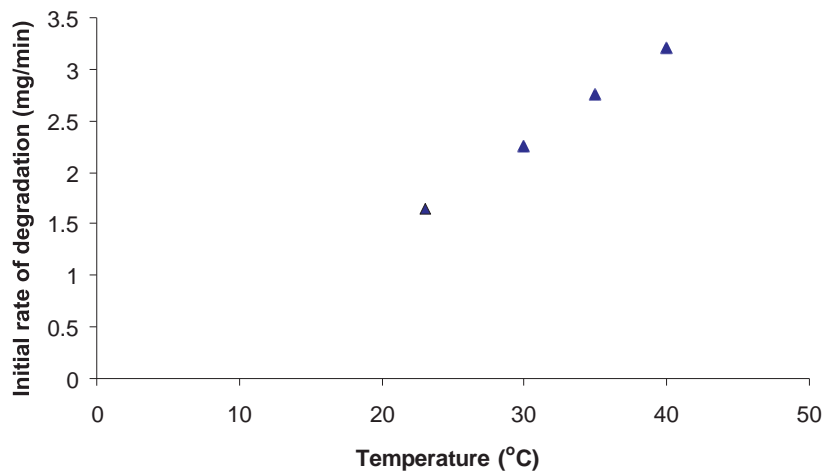


Figure 5. Initial rate of degradation of chlorendic acid as a function of temperature.

Linear transform of reciprocal initial rate vs. reciprocal equilibrium concentration

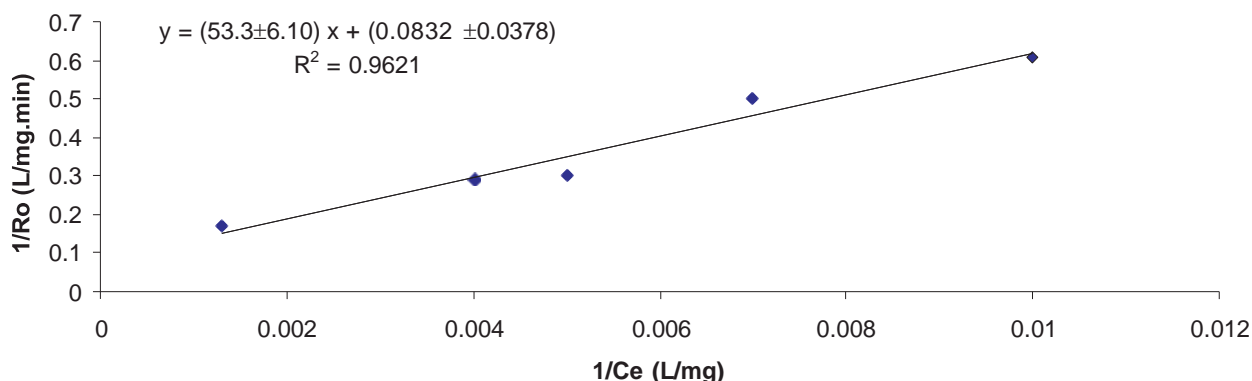


Figure 6. Plot of inverse of initial rate against inverse of equilibrium concentration. Experiment conducted at 25°C using TiO₂ (5 g/L) in 200 solution. Equilibrium concentration used: 105, 143, 199, 240 and 740 mg/L.

substrates and intermediates from the catalyst at higher temperatures, leading to larger effective surface area for the reaction have previously been reported (Carp et al., 2004; Al-Rasheed and Cardin, 2003). The decrease in the concentration of the chlorendic acid could be accounted for by a Langmuir-Hinshelwood Kinetic model:

$$R = k\theta = \frac{kKCe}{1+KCe}, \quad \text{Linear form: } \frac{1}{R} = \frac{1}{k} + \frac{1}{kK} \frac{1}{Ce}.$$

Where: R is the oxidation rate of the acid, θ the surface coverage, k the apparent rate constant. The value of the rate constant k, 12.0 ± 1.38 mg/L.min was estimated from Figure 6 with a correlation coefficient of 0.9621.

Conclusion

Heterogeneous photocatalytic degradation of chlorendic acid using UV-irradiation and TiO₂ (Degussa P-25) have been achieved. The quantity of TiO₂ that produced highest rate of removal was obtained at a concentration of 2 g/L. Temperature increase enhances the photocatalytic degradation of chlorendic acid TiO₂. Degradation kinetics of chlorendic acid in water is first-order and it follows the Langmuir-Hinshelwood model with kinetic constant k, 12.02 ± 1.38 mg / L.min.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

REFERENCES

- Al-Rasheed R, Cardin DJ (2003). Photocatalytic degradation of humic acid in saline waters. Part 1. Artificial seawater: influence of TiO₂, temperature, pH, and air-flow. *Chemosphere* 51(9):925-933.
- Boisa ND (2013). Photo-catalytic Degradation of Chlorendic Acid: 1. Degradation Products. *Journal of Applied Sciences and Environmental Management*. 17(3):335-340.
- Carp O, Huisman CL, Reller A (2004). Photoinduced reactivity of titanium dioxide. *Progress in solid state chemistry*. 32(1-2):33-177.
- Cochrane WP, Forbes MA (1974). Oxidation products of heptachlor and its metabolites--a chemical study. *Chemosphere*.
- He Z, Yang S, Ju Y, Sun C (2009). Microwave photocatalytic degradation of Rhodamine B using TiO₂ supported on activated carbon: Mechanism implication. *Journal of Environmental Sciences* 21(2):268-272.
- Honda K (2004). Dawn of the evolution of photoelectrochemistry. *Journal of Photochemistry and Photobiology A: Chemistry* 166(1-3):63-68.
- Rashed MN, El-Amin AA (2007). Photocatalytic degradation of methyl orange in aqueous TiO₂ under different solar irradiation sources. *International Journal of Physical Sciences*. 2(3):73-81.
- Schulte-Hostede S, Gäb S, Korte F (1978). Ozonisierung chlorierter Bicyclo [2.2. 1] hept-2-en-Derivate. *Chemische Berichte*. 111(7):2646-2655.
- Segev O, Kushmaro A, Brenner A (2009). Environmental impact of flame retardants (persistence and biodegradability). *International Journal of Environmental Research and Public Health* 6(2):478-91.
- Stowell JP, Jensen JN (1991). Dechlorination of chlorendic acid with ozone. *Water Research* 25(1):83-90.