



Study on the photocatalytic degradation of styrene using TiO₂ nanocatalyst

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Abstract

In the present study, photocatalytic degradation of styrene was evaluated using nano TiO₂ (Degussa P-25) as a catalyst. The experiments were conducted in a slurry batch reactor equipped with three UV lamps. Determinations of styrene concentrations were done by HPLC. Preliminary tests were made to determine the necessary contact time to reach the adsorption equilibrium. In addition to photocatalysis, separate photolysis experiments were conducted but showed low efficiency. For the photocatalysis experiments, the effects of the styrene initial concentration were evaluated, as well as, the catalyst concentration and the initial pH of the solution. The experimental results showed that in 125 min, 99% of the initial styrene was degraded by photocatalysis. It was verified that the styrene degradation rate fits a pseudo-first-order kinetics for initial styrene concentrations (100-200-300 ppm), at 25 °C. Optimal experimental conditions for arbitrary aqueous styrene concentration (100 mg L⁻¹) were found initial pH 6 and TiO₂ loading 1.0 gL⁻¹.

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Introduction

Styrene is potentially present in food, drinking water, indoor air or the environment as a result of direct releases or leaching of residual monomer from polymers. This toxic compound has a detrimental effect on wildlife and marine organisms, and it is potentially carcinogenic (Gibbs *et al.*, 1997).

In spite of its toxicity, the literature dealing with styrene photocatalytic degradation is scarce. Few articles regarding gas-phase photocatalytic oxidation of styrene in a tubular reactor and in a fluidized-bed

(Johnson *et al.*, 2009) are available, but nothing regarding contaminated wastewater is available. Styrene solubility in water is 300 mg L⁻¹ (20 °C), and its vapor pressure is 5 mm Hg at 20 °C and 1 atm (Gibbs *et al.*, 1997). These solubility characteristics allow styrene to be a major pollutant in water. The most important physicochemical properties of styrene are presented in Table 1. National Toxicology Program U.S (NTP) Estimated half-lives of styrene in surface waters range from 1 h in a shallow body of water to 13 days in a lake. The half-life of styrene in ground water is estimated at 4-30 weeks.

Table 1. some physicochemical properties of styrene (Keith and Walters, 1987).

Properties	value
Common Synonyms	vinyl benzene; phenylethene; ethenyl benzene
Molecular formula	C ₈ H ₈
Molecular Weight	104.14
Density	0.9059 g/mL (20°C)
Melting point	-30.6 °C
Boiling point	145-146 °C
Physical State	colorless to yellowish oily liquid

Photocatalysis is one of the advanced oxidation processes and is based on the formation of the HO[•] radical, a highly oxidizing agent. There are many studies in the literature dealing with wastewater photocatalytic treatment. Efforts are underway for dealing with dyes (Soares *et al.*, 2007) as well as water polluted with fungicides (Lhome *et al.*, 2007; Prestes *et al.*, 2010) antibiotics (Elmolla *et al.*, 2010; Mouamfon *et al.*, 2011) and insecticides (Guzsvány *et al.*, 2009), among other toxic molecules (Jo *et al.*, 2011).

In this study, the photocatalytic degradation of styrene in water was investigated using TiO₂ as a catalyst. The goals were (i) to evaluate the kinetics of styrene disappearance and (ii) to examine the effect of several parameters including catalyst mass, initial styrene concentration and pH change.

Materials and methods

Reagents

Titanium dioxide P-25 (Degussa) was used as a catalyst. This product contains 80% anatase and 20% rutile, and has a specific surface area of 50 m² g⁻¹ and a particle size of 21 nm. Other chemicals were purchased from Merck (Darmstadt, Germany) with a purity of >99% and deionized laboratory water was used for making aqueous mixtures. Initial pH of the solution was adjusted by using 0.1N NaOH and 0.1N HCL.

Photocatalytic reactor

The experiments were carried out in a 1000mL cylindrical stainless steel reactor (9 cm ID×25 cm H). The reactor was equipped with three UV-C lamps (F6T5/GL 6W, low pressure Hg lamp close to monochromatic output at 254 nm, Philips, Poland).

The UV light sources were surrounded by a Quartz glass tube to preventing direct contact with solution.

Photodegradation tests

Styrene solutions were prepared and maintained under agitation, after that pH was adjusted if necessary. The reactor was charged with 1000 mL of styrene solution and TiO₂. Each experiment was accomplished using agitation and constant temperature. Before each photodegradation experiment, the UV lamp was preheated for 30 min to obtain a constant light intensity during the tests. Suspensions of the photocatalyst and aqueous contaminant solutions were kept aerated and stirred by a steady stream of air to improve contact between styrene molecules and TiO₂ particles and maintain homogeneity. Sample collections were done using a syringe, and the samples were then centrifuged for catalyst removal. A 5 mL aliquot was collected after 0, 5, 10, 20, 35, 65, 95, and 125 min of reaction time.

Analysis

The concentration of Styrene in the aqueous solutions was measured by HPLC (Adept, Cecil Instruments, UK) equipped with a reverse-phase C18 Hichrom column (5µm, 4.6×150mm). The mobile phase was 75% acetonitrile and 25% water. Styrene concentration was determined using an injection volume of 20 µl at 245 nm wave length (UV detector) and a mobile phase flow rate of 1 ml/min.

Results and Discussion

Styrene degradation

It was necessary to evaluate the styrene lost to the atmosphere under the test conditions. Five tests were carried out without TiO₂ and with UV light. It was observed that the styrene loss to the environment is a reproducible phenomenon and has a minor role. Fig.1 shows that non-appreciable styrene photodegradation occurs after 125 min of irradiation without TiO₂ (photolysis). The photolysis results presented in this Figure had been corrected: the amount of styrene lost to the atmosphere was added point to point, in order to allow that each process is visualized individually.

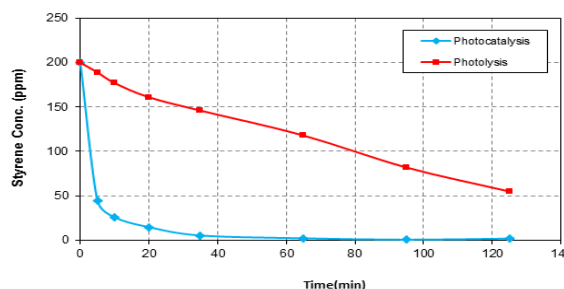


Fig. 1. Styrene concentration with time (T = 25 °C, C₀ = 200 ppm, C_{cat} = 0.1 g L⁻¹).

On the other hand, when the styrene solution mixed with TiO₂ was exposed to UV radiation, a fast decrease in the styrene concentration occurred, and 99% degradation for an initial concentration of 200ppm was reached in 125 min. Therefore, it can be concluded that styrene degradation in photocatalysis proceeds by the oxidation of styrene by hydroxyl radical. Pseudo-first-order reaction has been widely and successfully used for the description of photocatalytic degradation of organic pollutants. The removal rates of styrene in UV/TiO₂ process is therefore expressed as:

$$-Ln\left(\frac{C}{C_0}\right) = K_{ap}t$$

(1)

where, C₀ is the initial concentration of styrene, C the concentration at time t and K_{ap} (min⁻¹) is the pseudo-first-order photocatalytic removal rate constant.

Effect of initial styrene concentration

The styrene initial concentration effect (100, 200 and 300 ppm) was evaluated. The results are presented in Fig. 2, which shows the concentration against irradiation time for several styrene initial concentrations.

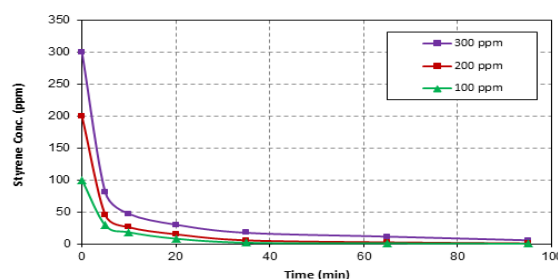


Fig. 2. The effect of initial styrene concentration on the photodegradation rate (T = 25 °C, and C_{cat} = 0.1 g L⁻¹).

Increasing styrene concentration decreases its degradation rate. Similar results have been presented for the photocatalytic oxidation of other organic compounds (Aliabadi and Sagharigar, 2011; Gautam *et al.*, 2005). According to Ishiki *et al* this decrease may be due to the fixed active site number at the TiO₂/H₂O interface. Therefore, at low styrene concentrations, a larger number of water molecules will be adsorbed onto the available TiO₂ particles, producing hydroxyl radicals and leading to a rapid oxidation process. On the other hand, at higher styrene concentrations, there is a smaller ratio of water molecules to free active sites, because the number of active sites remains the same. Consequently, competitive adsorption between the styrene and water molecules increases and leads to a decrease in the degradation rate.

Effect of catalyst concentration

The effect of the catalyst concentration in the mixture is shown in Fig. 3, which presents normalized styrene concentration against irradiation time. Furthermore the values of the pseudo-first-order apparent kinetic constant for several initial catalyst concentrations are presented in Table 2. The reaction kinetic constant increases as the catalyst concentration is incremented from 0.1 to 1.0 gL⁻¹. Similar behavior was observed by several authors for different pollutants (Barakat *et al.*, 2005; Andreozzi *et al.*, 2000). With the increased amount of catalyst, the number of photons absorbed and the number of molecules adsorbed also increased, due to an increase in the number of TiO₂ particles. The density of particles in the area of illumination also increased, and the degradation rate therefore increased.

As stated above, the optimum amount of catalyst loading was found to be 1.0 gL⁻¹ for the degradation of styrene. Hence, this amount was selected as the optimum value for further experiments.

Effect of initial pH

The efficiency of photocatalytic degradation is affected by the TiO₂ surface properties, the molecules

charge and the hydroxyl radical concentration. These properties depend on the solution pH. The effect of pH on styrene photocatalytic degradation was evaluated in this study. Fig. 4 and Table 3 show the degradation rate and apparent pseudo-first-order kinetic constant values for several initial pH conditions. Electrostatic attraction or repulsion between the catalyst surface and the organic molecule depends on the ionic form of the organic compound (anionic or cationic) and the surface charge (Evgenidou *et Al.* 2005). The electric charge of a solid surface in an aqueous solution is determined by the zero point charge (ZPC). At pH values lower than ZPC, the catalyst's surface is positively charged, and at higher pH values it is negatively charged. The ZPC of the TiO₂ catalyst (Degussa P25) is pH 6.8 (Zhang *et al.*, 1998; Guillard *et al.*, 2003).

Table 2. The pseudo-first order reaction rate constants for the photocatalytic degradation of styrene at various catalysts loading.

Catalyst Loading	K _{ap}	R ²
0.1 g/l	0.033	0.801
0.3 g/l	0.057	0.942
0.5 g/l	0.054	0.908
1.0 g/l	0.062	0.902

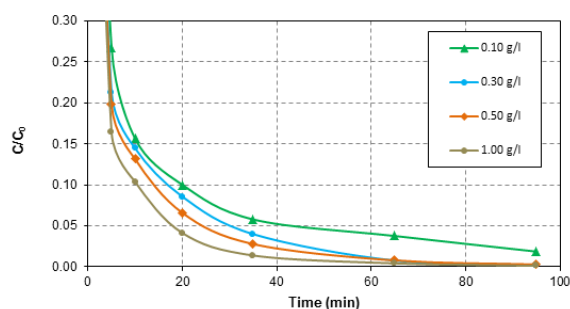


Fig. 3. Effect of TiO₂ loading on the photocatalytic degradation of styrene (T = 25 °C, C₀ = 300 ppm).

Fig. 4 shows that the reaction presented a maximum degradation rate at pH 6.0 (the natural pH of solution). At pH 6.0, the TiO₂ surface was weakly charged (near ZPC), a situation in which molecules probably reach the catalyst surface more easily. This phenomenon facilitates the adsorption of the

pollutant and consequently permits the degradation rate to reach its maximum value (Evgenidou *et al.* 2005; Subramanian *et al.* 2000). On the other hand, at basic pH, the TiO₂ surface is negatively charged (TiO⁻), and the Na⁺ ions adsorption competes with organic molecule adsorption. Moreover, in the alkaline solution there is repulsion between the negatively charged surface of photocatalyst and the hydroxide anions. This repulsion could prevent the formation of HO[•] and thus decrease the rate of photooxidation (Konstantinou and Albanis, 2004).

Table 3. Effect of initial pH on the styrene degradation rate constant.

Initial pH	K _{ap}	R ²
3	0.030	0.973
5	0.026	0.947
6	0.032	0.855
9	0.021	0.940
11	0.016	0.859

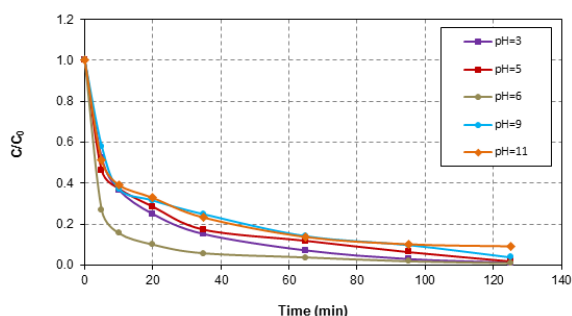


Fig. 4. Effect of solution pH on the photocatalytic degradation of styrene (C₀ = 300ppm, C_{cat} = 0.1 g L⁻¹, T = 25 °C).

Conclusions

The photocatalytic degradation of styrene in aqueous solution was studied in a bath slurry reactor irradiated with UV light sources and using titanium dioxide as a catalyst. Under experimental conditions, it was found that styrene degradation is mainly due to photocatalytic process because in the absence of either the catalyst or UV radiation, removal rate was negligible. The results of experiments showed that styrene degradation kinetics can be approximated by a pseudo-first order model with a reaction rate

dependent on the initial concentration of styrene, the TiO₂ concentration, and solution pH. The degradation rate decreased with increasing initial concentrations of styrene, and it increased with increasing catalyst concentrations up to a maximum of 1.0 g L⁻¹. Additionally, the degradation rate was maximal when the pH was approximately 6. Finally, it can be concluded that UV/TiO₂ process can be used successfully for the treatment of styrene containing wastewater.

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