

Heterogeneous photocatalytic degradation of *p*-toluenesulfonic acid using concentrated solar radiation in slurry photoreactor

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Abstract

In this work, the photocatalytic degradation (PCD) of *p*-toluenesulfonic acid (*p*-TSA) in batch reactor using concentrated solar radiation was investigated. The effect of the various operating parameters such as initial concentration of substrate, catalyst loading, solution pH and types of ions on photocatalytic degradation has been studied in a batch reactor to derive the optimum conditions. The rate of photocatalytic degradation was found to be maximum at the self pH (pH 3.34) of *p*-TSA. It was also observed that in the presence of anions and cations, the rate of PCD decreases drastically. The kinetics of photocatalytic degradation of *p*-TSA was studied. The PCD of *p*-TSA was also carried at these optimized conditions in a bench scale slurry bubble column reactor using concentrated solar radiation.

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1. Introduction

Environmental pollution by chemical substances has become a serious problem throughout the world. Aromatic sulfonated compounds are one major class of pollutants. Alkylbenzenesulfonates are important components of surfactants and frequently cause water pollution. These compounds have low volatility and are relatively more water soluble and hence often found in aqueous effluents. In this investigation, *p*-toluenesulphonic acid (*p*-TSA) was chosen, as a model compound representative of alkylbenzenesulfonic acids. *p*-TSA is very corrosive and is extremely harmful to tissues of the mucous membranes and upper respiratory tract. For anhydrous *p*-TSA: oral-mouse; LD₅₀: 400 mg kg⁻¹. The degradation of *p*-TSA by biological methods is difficult; this may be due to the sulfonic acid functional group, which generally impairs biodegradability of organics and at the same time might enhance polarity. Therefore, *p*-TSA is considered as a refractory compound [1].

The photocatalytic degradation of many types of anionic, cationic and non-ionic surfactants using artificial UV light and solar radiation has been reported by Hidaka and co-workers [2–4]. Recently few studies have been reported on degradation of aromatic sulfonated compounds using advanced oxidation processes [5–9]. A few research articles have also been published particularly on destruction of *p*-TSA in aqueous solutions mainly by using (i) immobilized TiO₂ and (ii) active hydrogen peroxide [1,10].

Heterogeneous photocatalysis offers an attractive alternative for wastewater treatment especially refractory aromatic compounds. Despite the great potential of photocatalytic process, it has not widely used industrially. The problems which have restricted widespread commercialization of this attractive technology to date are the material handling problems presented by the fine particulate nature of TiO₂ and the fact that the polar surface of TiO₂ is not favorable for adsorption of organics in competition with water. As a result, no commercial application of TiO₂ photocatalysis to aqueous waste streams has yet emerged. Therefore, more research work is needed (i) on development of novel catalyst, particularly for catalyst, which are excited by visible radiation (although some reports are available on the same), (ii) design of efficient photocatalytic reactor for wastewater treatment.

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Nomenclature

| | |
|----------------------|---|
| C | concentration of substrate at time t (mg l^{-1}) |
| C_0 | initial concentration of the substrate (mg l^{-1}) |
| $C_{t=0}$ | concentration of substrate at time $t=0$, before the p -toluenesulfonic acid solution was exposed to sunlight (mg l^{-1}) |
| k_{ap} | apparent reaction rate constants (min^{-1}) |
| $k_{\text{L-H}}$ | reaction rate constant ($\text{mg l}^{-1} \text{min}^{-1}$) |
| K_{ads} | adsorption coefficient of p -TSA on the TiO_2 particles (mg^{-1}) |
| R | reaction rate ($\text{mg l}^{-1} \text{min}^{-1}$) |
| TOC | total organic carbon after time t (mg l^{-1}) |
| $(\text{TOC})_{t=0}$ | total organic carbon at time t , before the p -TSA solution was exposed to sunlight (mg l^{-1}) |

Kamble et al. [7] have discussed the main problems associated with the large scale use of PCD and have suggested that a novel slurry bubble column reactor using concentrated solar radiation can be effectively used for industrial applications. Hence the same type of reactor was used in the present investigation.

The aim of the present work was to study the photocatalytic degradation (PCD) of p -TSA in batch and continuous slurry bubble column reactor using concentrated solar radiation. The effects of the presence of anions, which are commonly present in industrial wastewaters, are reported. The effect of pH on the photocatalytic degradation of p -TSA was also studied. The kinetics of photocatalytic degradation of p -TSA was also studied. No literature studies are available on these parameters on photocatalytic degradation of p -TSA in the published literature.

2. Experimental

2.1. Materials

P-25 TiO_2 was procured from Degussa Co., Germany, was used as photocatalyst. p -TSA, p -cresol, sodium chloride, sodium carbonate, sodium bicarbonate, sodium sulfate, ammonium sulfate, ferrous sulfate and copper sulfate of analytical reagent grade were obtained from s.d. fine chemicals Ltd., Mumbai, India. Other accessories required for experimentation were the same as reported previously by Kamble et al. [7].

2.2. Batch experiments

The equipment and procedure used has been described elsewhere [7,11].

2.3. Continuous experiments

Continuous experiments were carried out in borosilicate glass slurry bubble column reactor of 0.15 m i.d. \times 3.0 m long and capacity of 0.054 m^3 [11].

2.4. Analysis

In all photocatalytic experiments, samples were centrifuged and filtered through a membrane filter to separate out TiO_2 particles. Concentrations of p -TSA and its intermediates were measured by an HPLC (Knauer) instrument equipped with a C-18 column (5 μm , particle diameter, Merck) and UV-vis detector. Acetonitrile/water: (50:50%, v/v) was used as the mobile phase; the pH of the mobile phase was adjusted to 3 with the help of HClO_4 for separation of p -TSA and its intermediates. The flow rate of mobile phase for analysis was kept at 0.5 ml min^{-1} using $\lambda = 240 \text{ nm}$ for UV detector. Total organic carbon (TOC) was calculated from HPLC analysis and verified using a Total Organic Carbon Analyzer (ANATOC-II, Australia). These values matched within $\pm 3\%$ indicating that the HPLC analysis could detect all of the intermediates. Pure nitrogen was bubbled through the samples before TOC analysis to remove the dissolved CO_2 . In case of carbonate and hydrogen carbonate the samples was acidified prior to purging. The intermediates were further confirmed by spiking the experimental samples with authentic compounds. Increase in concentration on spiking confirmed the presence of the particular compound as an intermediate.

3. Results and discussion

The experiments were carried out in the month of January–April 2004 in Mumbai, India 18.58°N, and 72.50°E. During this period the sky was brilliant blue (no clouds) and the average solar intensity was approximately ($\pm 10\%$) constant at 820 W m^{-2} as measured at the ground level. This intensity is referred to as the plain solar intensity.

3.1. Mechanism of photocatalytic degradation of p -TSA

There is evidence supporting the proposition that the hydroxyl radical (OH^\bullet) is the main oxidizing species responsible for photocatalytic oxidation of the majority organic compounds [12,13]. In aqueous TiO_2 suspensions, aromatic compounds are oxidized through two different mechanisms; either by hydroxylation of the aromatic ring or by direct electron transfer to TiO_2 followed by the addition of a water molecule and loss of a proton. In the case of aromatic compounds the position at which OH^\bullet attacks depends on the directing effect of the original functional group in the benzene ring. Several studies on the mechanism photocatalytic degradation of aromatic substrate are available [13].

In the case of p -TSA, the SO_3H group is replaced by an OH^\bullet radical. During the photocatalytic degradation of p -TSA, p -cresol was found as intermediate. Identification of p -TSA and its intermediates was carried out by comparison of their retention times with those of authentic standards. The HPLC measurements were conducted by monitoring the UV absorption at wavelength 240 nm. By comparing HPLC and spectral data, the aromatic intermediate was identified as p -cresol, however the concentration of these intermediates was very low ($1\text{--}5 \text{ mg l}^{-1}$). p -Cresol was detected within the first hour of exposure to sun-

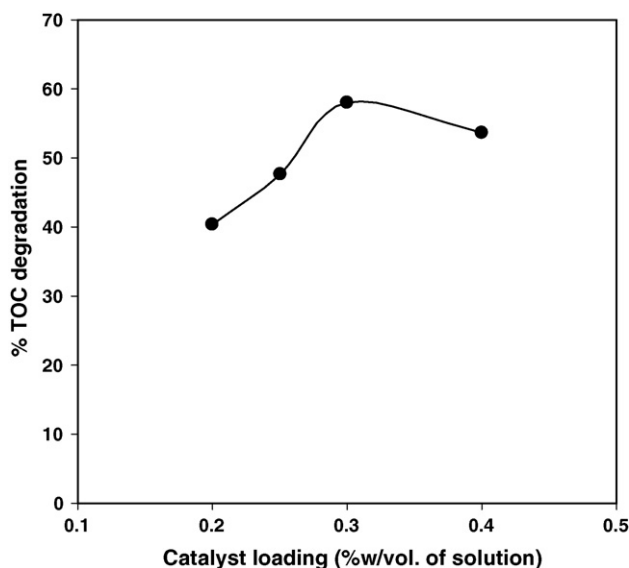


Fig. 1. Influence of catalyst loading on photocatalytic degradation of *p*-TSA [$\text{TOC}/(\text{TOC})_{t=0}$ vs. time].

light, which demonstrates that, it has close relationship with the parent compound. This intermediate was also observed during the photochemical degradation of *p*-TSA by Brezova et al. [10]. It is known that the aromatic ring yields at the most trihydroxy derivatives. Generally after the attachment of two OH^\bullet groups the aromatic ring breaks. The subsequent products are rapidly oxidized to CO_2 and H_2O as evidenced by the absence of aliphatic moieties [13].

3.2. Batch photocatalytic degradation with concentrated solar radiation

3.2.1. Influence of catalyst concentration on photocatalytic degradation of *p*-TSA

In slurry photocatalytic processes, the TiO_2 dosage is an important control parameter that can affect the degradation rate [14]. As the catalyst loading is increased, there is an increase in the surface area of the catalyst available for adsorption and degradation. But when the catalyst concentration is very high, turbidity impedes further penetration of light into the reactor. Therefore, optimum catalyst loading has to be found to avoid excess catalyst and ensure effective utilization of the incident photons.

With an initial concentration of 100 mg l^{-1} of *p*-TSA, the optimum loading of the catalyst was found by varying the catalyst loading. As can be seen from Fig. 1 the optimum catalyst loading is 0.3% (w/v of the solution). In all subsequent experiments, 0.30% (w/v of the solution) TiO_2 loading was used.

3.2.2. Effect of initial concentration of *p*-TSA

Photocatalytic degradation studies were carried out using 50, 100 and 200 mg l^{-1} initial concentration of *p*-TSA and 0.30% (w/v of solution) catalyst loading.

Fig. 2 shows a plot of normalized concentration of *p*-TSA ($C/C_{t=0}$) with time. With increasing initial *p*-TSA concentration,

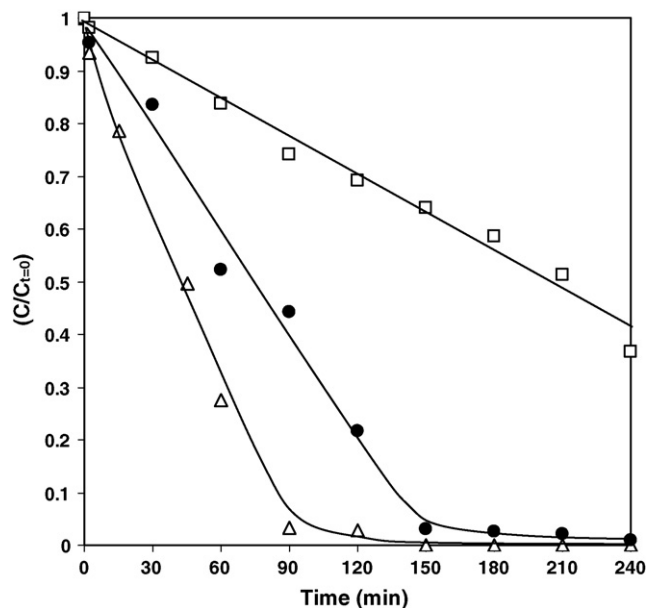


Fig. 2. Effect of initial concentration on the photocatalytic degradation of *p*-TSA [$\ln(C_0/C)$ vs. time]. Catalyst loading = 0.30% (w/v of solution). Initial concentration (Δ) 50 mg l^{-1} , (\bullet) 100 mg l^{-1} and (\square) 200 mg l^{-1} .

the *p*-TSA concentration was reduced by 99.9%, 99% and 63.3%, respectively, within 4 h; while the TOC was by reduced 94.7%, 65.4% and 46.4%, respectively, in the same period (Fig. 3).

Fig. 2 shows that an increase in the feed concentration of *p*-TSA causes decrease in the rate of photocatalytic degradation. As mentioned earlier the reaction occurs between adsorbed *p*-TSA and OH^\bullet generated on the TiO_2 surface. The concentration of adsorbed *p*-TSA increases with increasing feed *p*-TSA con-

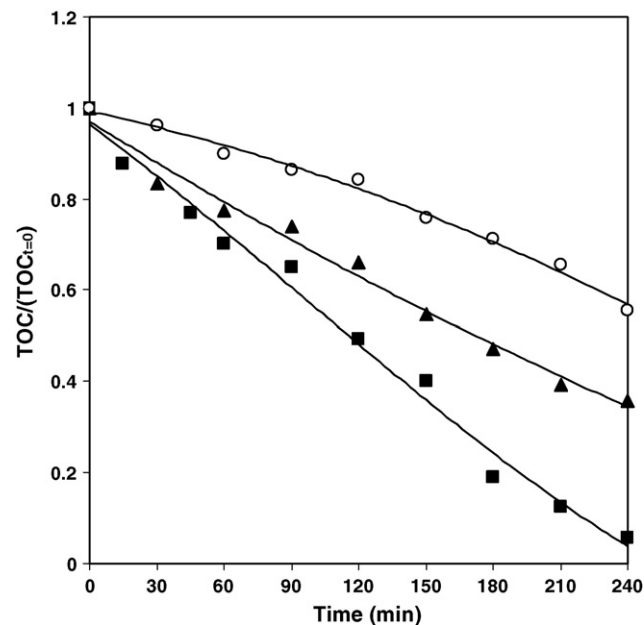


Fig. 3. Effect of initial concentration on the photocatalytic degradation of *p*-TSA [$\text{TOC}/(\text{TOC})_{t=0}$ vs. time]. Catalyst loading = 0.30% (w/v of solution). Initial concentration (\blacksquare) 50 mg l^{-1} , (\blacktriangle) 100 mg l^{-1} and (\circ) 200 mg l^{-1} .

centration, but at higher concentrations of *p*-TSA, the concentration of intermediates formed is higher. These intermediates adsorb on the surface of catalyst and compete with the parent compound. However, for constant light intensity, TiO₂ loading and dissolved oxygen concentration, the concentration of OH• remains practically constant.

3.2.3. Kinetics of photocatalytic degradation of *p*-TSA

The photocatalytic degradation kinetics of many organic compounds have been often described by Langmuir–Hinshelwood equation, which also covers the adsorption properties of the substrate on the photocatalyst surface. This model was developed by Turchi and Ollis [12] as given below:

$$R = -\frac{d[p\text{-TSA}]}{dt} = \frac{k_{L-H}K_{\text{ads}}[p\text{-TSA}]}{1 + K_{\text{ads}}[p\text{-TSA}]} \quad (1)$$

where *R* is the reaction rate (mg l⁻¹ min⁻¹), *k*_{L-H} the reaction rate constant (mg l⁻¹ min⁻¹), *K*_{ads} the adsorption coefficient of *p*-TSA on the TiO₂ particles (mg⁻¹ l) and [*p*-TSA] is the concentration of *p*-toluenesulfonic acid (mg l⁻¹). Reaction intermediates (for example *p*-cresol) can also bind competitively to the catalyst active sites, and their concentrations also change with time, inasmuch as they are eventually and completely mineralized. Al-Ekabi and Serpone [15] have suggested that the rate must include competitive adsorption by intermediates. Under these reasonable conditions Eq. (1) can be written as follows:

$$R = -\frac{d[p\text{-TSA}]}{dt} = \frac{k_{L-H}K_{\text{ads}}[p\text{-TSA}]}{1 + K_{\text{ads}}[p\text{-TSA}] + \sum K_i C_i} \quad (2)$$

In this equation, *K*_{*i*} and *C*_{*i*} are the adsorption equilibrium constant and concentration for intermediates, respectively. Beltran-Heredia et al. [16] made the following assumption:

$$K_{\text{ads}}[p\text{-TSA}] + \sum K_i C_i = K_{\text{ads}}[p\text{-TSA}]_0 \quad (3)$$

In this equation, [*p*-TSA]₀ is the initial concentration of *p*-TSA. Substituting Eq. (3) in to Eq. (2) yields:

$$R = -\frac{d[p\text{-TSA}]}{dt} = \frac{k_{L-H}K_{\text{ads}}[p\text{-TSA}]}{1 + K_{\text{ads}}[p\text{-TSA}]_0} = k_{\text{ap}}[p\text{-TSA}] \quad (4)$$

where

$$k_{\text{ap}} = \frac{k_{L-H}K_{\text{ads}}}{1 + K_{\text{ads}}[p\text{-TSA}]_0} \quad (5)$$

Eq. (4) shows a pseudo-first order reaction with respect to the *p*-TSA concentration. The semi-logarithmic graphs of the concentration of *p*-TSA in the presence of different concentrations of *p*-TSA versus irradiation time yield straight lines indicating pseudo-first order reaction. The apparent reaction rate constants (*k*_{ap}) for photocatalytic degradation of *p*-TSA were evaluated from experimental data (Fig. 2) using a linear regression. At initial concentration of 50, 100 and 200 mg l⁻¹ of *p*-TSA, the value of *k*_{ap} are 0.003, 0.0182 and 0.0278 min⁻¹, respectively. In all cases, *R*² (correlation coefficient) values are higher than 0.96, which confirm the proposed kinetics for photocatalytic degradation of *p*-TSA in TiO₂ solution.

3.2.4. Effect of pH

The effect of initial pH on the photocatalytic degradation of *p*-TSA was studied. In the alkaline range, the pH was varied using aqueous NaOH, whereas in the acidic range, it was varied by using HClO₄. Initial *p*-TSA concentration of 100 mg l⁻¹ and catalyst loading of 0.30% (w/v of solution) was used in all these experiments. It is known that, in photocatalytic reactions pH has an effect on the electrostatic charge of the TiO₂ surface, which determines the density of TiOH₂⁺ groups. Consequently, the adsorption of organic substrate with functional groups like the SO₃H, which are dissociated in aqueous media on TiO₂ and the photocatalytic reactivity of TiO₂, could be affected when pH changes. Also, industrial effluents may be basic or acidic and therefore this pH effect needs to be investigated.

Fig. 4 shows a plot of normalized concentration of *p*-toluenesulfonic acid (*C/C*_{*t*=0}) with time. It is observed that as the pH increases from acidic to alkaline the rate of PCD is a maximum at the non-adjusted or “self pH” (3.34). Fig. 5 shows a plot of normalized total organic carbon concentration [TOC/(TOC)_{*t*=0}] with time at different pH. It is observed that as the pH decreases from alkaline to acidic the rate of photocatalytic mineralization of *p*-TSA also increases and is maximum at pH 3.34. Similar results were obtained in the photocatalytic degradation of benzenesulfonic acid [7], 2,4-D [11].

3.2.5. Effect of the presence of anions

Industrial effluents contain apart from pollutants different salts at different levels of concentration. The anionic and cationic parts of the salt have different effects on the photocatalytic degradation process [13]. The effects of presence of various anions

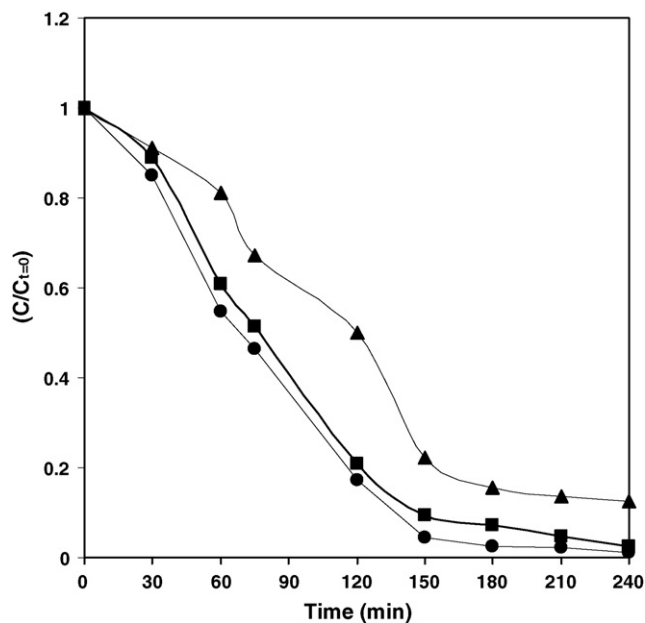


Fig. 4. Effect of pH on the photocatalytic degradation of *p*-TSA on TiO₂ [(*C/C*_{*t*=0}) vs. time]. Initial concentration = 100 mg l⁻¹, catalyst loading = 0.30% (w/v of solution). (●) pH 3.34, (■) pH 7.0 and (▲) pH 11.0.

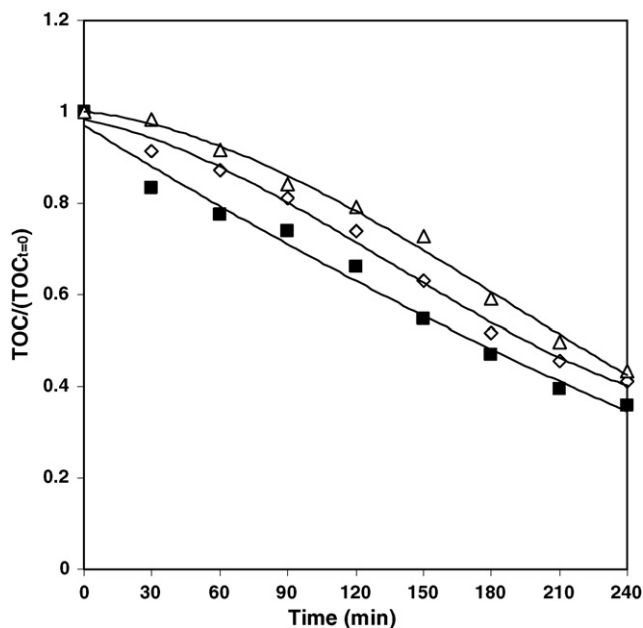


Fig. 5. Effect of pH on the photocatalytic degradation of *p*-TSA on TiO₂ [TOC/(TOC)_{t=0} vs. time]. Initial concentration = 100 mg l⁻¹, catalyst loading = 0.30% (w/v of solution). (■) pH 3.34, (◇) pH 7.0 and (△) pH 11.0.

such as chloride, sulfate, bicarbonate and carbonate were studied using 0.1 M solution of their sodium salts and initial concentration of 100 mg l⁻¹ of *p*-TSA with 0.30% (w/v of solution) TiO₂ loading.

In general an effluent is brought to neutral pH before it is introduced in the effluent treatment plant (ETP). In the case of *p*-TSA the original solution being acidic, an alkali is added to raise the pH to the neutral pH. Fig. 6 shows the effect of the salts on the photocatalytic degradation *p*-TSA. Fig. 6 clearly indicates that the salts have a substantial detrimental effect on the photocatalytic degradation. In the case of sodium sulfate, sodium chloride, sodium bicarbonate and sodium carbonate the reduction in the TOC was 62%, 49.5%, 33.9% and 20.3%, respectively, whereas in the absence of anions the reduction in TOC was 99%. The rate of photocatalytic degradation was inhibited in the presence of bicarbonate and carbonate, this may be because of two reasons (i) there has been pH shift (from acidic to alkaline) which inhibits PCD (Fig. 4 also shows same trend) and (ii) bicarbonate and carbonate act as hydroxyl radical scavengers and also absorb UV light, which further inhibits the PCD. Previous studies with benzenesulfonic acid [7] and 2,4-D [11] have also concluded that all the above anions have a negative effect on photocatalytic degradation.

Thus, it can be concluded that if photocatalytic degradation is to be adopted for the treatment of acid wastewater containing *p*-TSA, it will be desirable to carry out the photocatalytic degradation prior to neutralization. The output of the photocatalytic degradation process can subsequently be introduced into the ETP.

3.2.6. Effect of cations

The presence of the various cations is common in industrial effluents. These cations can have a positive or negative

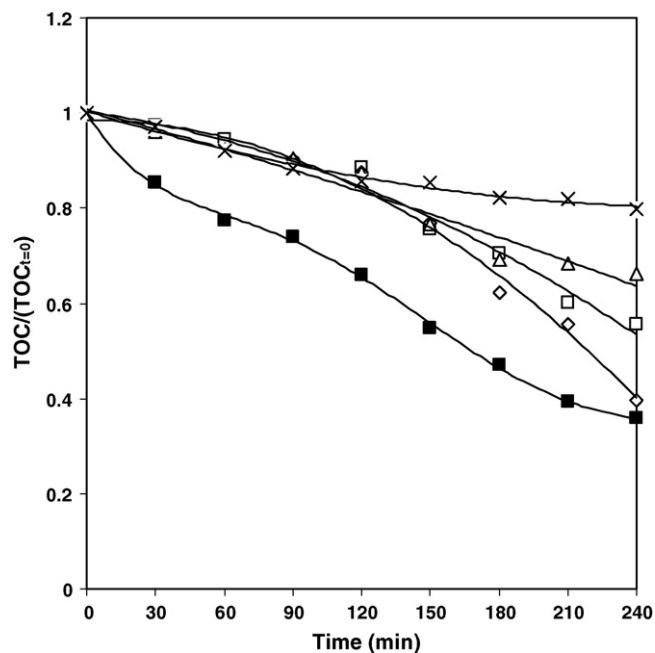


Fig. 6. Effect of the presence of the various anions on photocatalytic degradation of *p*-TSA on TiO₂ [TOC/(TOC)_{t=0} vs. time]. Initial concentration = 100 mg l⁻¹, catalyst loading = 0.30% (w/v of solution). (■) PCD of *p*-TSA in the absence of anions, (□) PCD of *p*-TSA in the presence of 0.1 M NaCl, (◇) PCD of *p*-TSA in the presence of 0.1 M Na₂SO₄, (△) PCD of *p*-TSA in the presence of 0.1 M NaHCO₃ and (×) PCD of *p*-TSA in the presence of 0.1 M Na₂CO₃.

effect on the PCD rate. Some researchers have reported an improvement in the PCD rate in the presence of low concentrations of FeSO₄ [13]. Therefore, the degradation of *p*-TSA was studied in the presences of 0.01 M solution of FeSO₄ and CuSO₄. It was found that the degradation of *p*-TSA in the presence of FeSO₄ and CuSO₄ decreased. Thus, the degradation of *p*-TSA in the presence of FeSO₄ and CuSO₄ was 14.9% and 32%, respectively, as against 88.6% in their absence (Fig. 7). It is likely that the positive effect of the cation is more than nullified by the negative effect of the SO₄²⁻ anion.

3.3. Continuous photocatalytic degradation in a slurry bubble column reactor with concentrated solar radiation

Continuous PCD experiments were performed in 0.15 m i.d. slurry bubble column reactor. Bubble columns exhibit significant axial mixing in the liquid phase. This mixing is detrimental to their performance as a reactor. Sectionalization of the bubble column can reduce the backmixing. In our previous publication we have shown that in the presence of sieve plates with downcomer in a bubble column, the percentage degradation of refractory pollutants increases [11]. The same experimental setup [11] was used for PCD of *p*-TSA solution. Fig. 8 shows the variation of extent of photocatalytic degradation of *p*-TSA at different flow rate in the slurry bubble column reactor. The rate of PCD and TOC degradation decreases with increase in the flow rate of *p*-TSA (decrease in residence time) as is evident from Fig. 8. Thus, only 35% degradation of *p*-TSA was achieved in

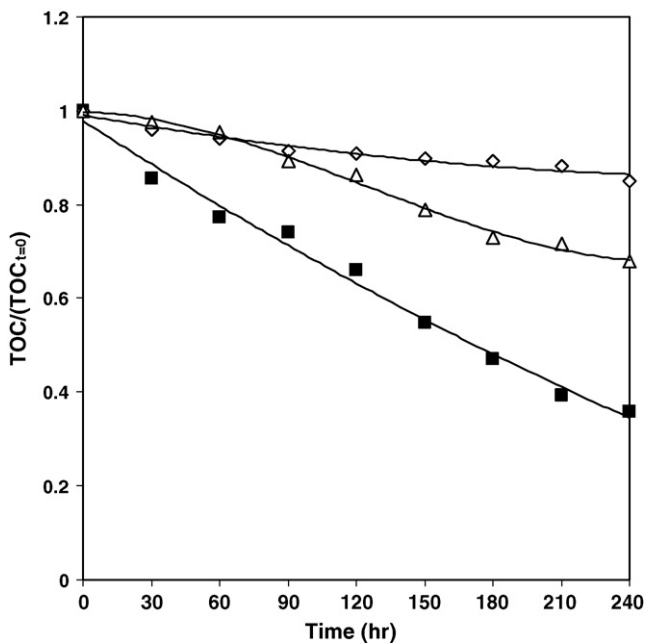


Fig. 7. Effect of the presence of the various cations on PCD of *p*-TSA on TiO₂ ($C/C_{t=0}$ vs. time). Initial concentration = 100 mg l⁻¹, catalyst loading = 0.30% (w/v of solution), (■) PCD of *p*-TSA in the absence of cations, (◇) PCD of *p*-TSA in the presence of 0.01 M FeSO₄ and (△) PCD of *p*-TSA in the presence of 0.01 M CuSO₄.

continuous slurry bubble column reactor. However, 96% and 75% degradations of chlorobenzene and nitrobenzene, respectively, were achieved in the 0.10 m i.d. slurry bubble column reactor [17]. Thus, the rate of PCD of *p*-TSA was low as compared to chlorobenzene and nitrobenzene. This is because the

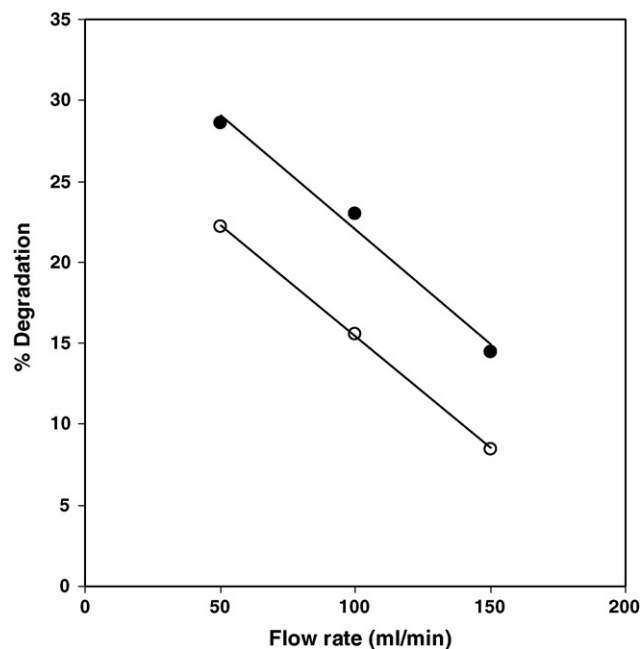


Fig. 8. Variation of the extent of the photocatalytic degradation *p*-TSA with sieve plate at different flow rate in 0.15 m slurry bubble column (Initial concentration = 100 mg l⁻¹, catalyst loading = 0.3, w/v of the solution). (●) %Degradation of *p*-TSA and (○) %TOC reduction.

adsorption of chlorobenzene and nitrobenzene on TiO₂ is very high as compared to *p*-TSA. Further, the surface area per unit volume for the 0.1 m i.d. reactor is higher than the 0.15 m i.d. reactor. Additionally, the penetration depth in the former is also lower than the latter [17].

4. Conclusions

Photocatalytic reactors can play an important role in novel technologies for the purification of water polluted with refractory organic chemicals. It was found that in the presence of ions such as CuSO₄, FeSO₄, Na₂CO₃ and NaHCO₃ have a deleterious effect on the photocatalytic degradation of *p*-TSA. Batch photocatalytic degradation studies indicate that *p*-TSA is best degraded under acidic pH conditions. Therefore, it is desirable to carry out the photocatalytic degradation of *p*-TSA before neutralization. The results obtained in the continuous slurry bubble column reactor are encouraging and for higher percentage degradation future research on development of novel visible photocatalyst and optimization of the reflector geometry is needed.

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