



DEGRADATION OF 2-TOLUIC ACID BY UV, UV/ H₂O₂ AND PHOTOFENTON PROCESSES

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Abstract:

The present study was used to probe the treatment of simulated wastewater containing 2-toluic acid by UV, UV/ H₂O₂ and photofenton processes. Experiments were conducted in a batch photoreactor to examine the effects of operating variables like pH, ratio of H₂O₂/COD, and different combinations of oxidizing agents with UV, and their degradation rate is compared. A pseudo-first order kinetic model was adopted to represent the photo-oxidative degradation of 2-toluic acid. The degradation rate of 2-toluic acid obeys the following sequence: photofenton (UV/Fe²⁺/ H₂O₂) > photoperoxidation(UV/ H₂O₂) > photolysis(UV).

Keywords: 2-toluic acid, photoperoxidation, photofenton, photolysis.

Introduction: In recent years, various studies have reported the occurrence of a large number of pharmaceuticals in surface water, but also in ground water. Surface water and ground water are widely used as water resources for drinking water. Therefore, the widespread occurrence of pharmaceuticals may have a negative impact on purity of drinking water. Complete removal or reduction of hazardous organic pollutants present in wastewater to an acceptable level prescribed by the environmental protection agencies is of prime importance in wastewater treatment. Advanced oxidation processes(AOPs) are the most promising technologies for destroying toxic organic contaminants(1-3).Consequently, AOPs are of high interest to the scientific and industrial communities involved in water treatment and have been successfully applied to the detoxification of water polluted with a wide variety of chemicals such as pesticides , phenols, hydrocarbons, surfactants, dyes and pharmaceutical wastes(4-10).



Toluic acid is produced from oil industry, petroleum refining, etc. It is used as a solvent carrier in paints, inks, thinners, coatings, adhesives, degreasers, pharmaceutical products, printing industry, leather finishing industry, rubber coating industry, shoemakers, etc. Decomposition of organic substances by photooxidation(11) is one of the most promising processes in water and wastewater treatments. In Fenton processes(12- 17); oxidants like peroxides are activated by relatively a non-toxic catalyst like iron at room temperature to oxidize the persistent organic compounds in clean and safe manner. The objective of this study is to degrade 2- toluic acid by AOP's like UV/ H₂O₂ and UV/Fe²⁺/ H₂O₂ and compare their degradation rates and to show that it follows a pseudo-first order kinetics.

2. Materials and methods

2.1 Chemicals

Analytical grade 2- toluic acid was purchased from Merck, India; and was used as received without any further purification and stock solution of 0.01M of 2- toluic acid was prepared. Initial concentration of 2- toluic acid used during the experimental runs was 0.08mM. Stock solution of H₂O₂ was prepared by diluting 30% w/v of peroxide (Qualigens) with distilled water. Analytical grade ferrous sulphate heptahydrate (FeSO₄.7H₂O, Merck) was used as a source of iron and the stock solution was maintained at 0.01mM in diluted sulphuric acid. All stock solutions were stored in amber colored light resistant pyrex glass bottles. Sodium hydroxide (1N) and sulphuric acid (1N) were used for pH adjustments.

2.2. Experimental procedure

Batch experiments were conducted at room conditions to determine the effect of pH, H₂O₂ concentration and Fe²⁺ ion concentration on degradation of 2- toluic acid. All experiments were conducted out in a photoreactor (Fig. 1) equipped with low pressure mercury lamp (8W, UV-C manufactured by Phillips,

Holland) placed in its centre. During the reaction, the solution was stirred by magnetic pellet to ensure its homogeneity.

Synthetic wastewater containing 0.08mM solution of 2- toluic acid in double distilled water was used in this study. 750 ml. of this synthetic wastewater was taken in the photoreactor and irradiated with UV lamp of 8W. Various experiments were carried out using UV light with oxidant at various stoichiometric ratios of oxidant/pollutant. The overall degradation reaction was carried out for 3h when H_2O_2 as oxidant and 1.5h when Fenton reagent was used.

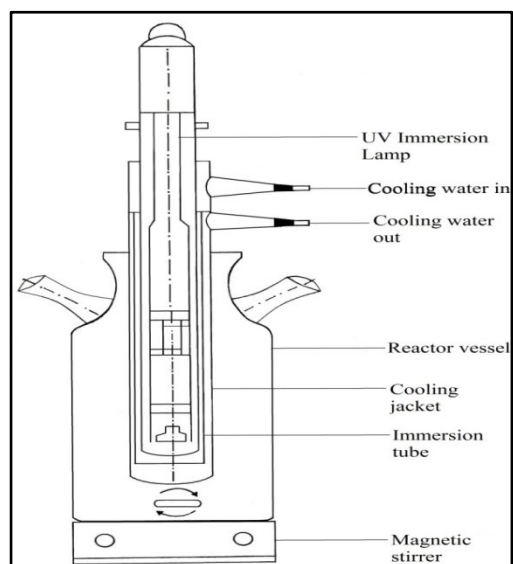


Fig. 1. Photoreactor

2.3. Analyses

The initial pH of the solution was measured using Elico pH meter LI-120 equipped with a combined calomel-glass electrode. The H_2O_2 concentration in the stock solution and in samples was determined by standard iodometric titration method described in Jeffery et al. (1989). The UV-visible spectrophotometric method was used for measurement of 2- toluic acid and H_2O_2 concentration in aqueous solution. A UV-visible spectrophotometer (Spectrascan UV 2600, Chemito, India) was used for this purpose. A calibration

plot between absorbance and concentration of 2- toluic acid was plotted experimentally, which gave a high linear regression coefficient of 0.999 at 228 nm. (Fig. 2).

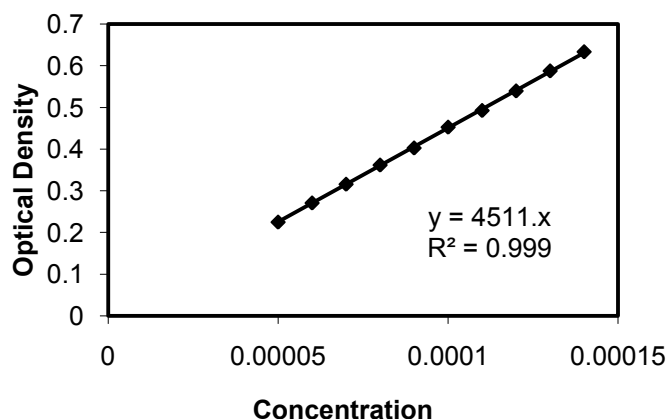


Fig. 2. Calibration plot of 2- toluic acid

3. Results & Discussion

The results of the various studies in the present investigation are presented subsequently.

3.1. Effect of pH

pH is one of the most important parameters to be studied. The rate of degradation of 2- toluic acid at different pH was observed by carrying out the experiments at different pH conditions namely plain water, 3, 4.5, 7 and 9.2. As depicted in the Fig. 3, in case of H_2O_2/UV , the maximum degradation of 2- toluic acid was achieved at pH 4.5 and shows decreasing trend of degradation at higher and lower pH.

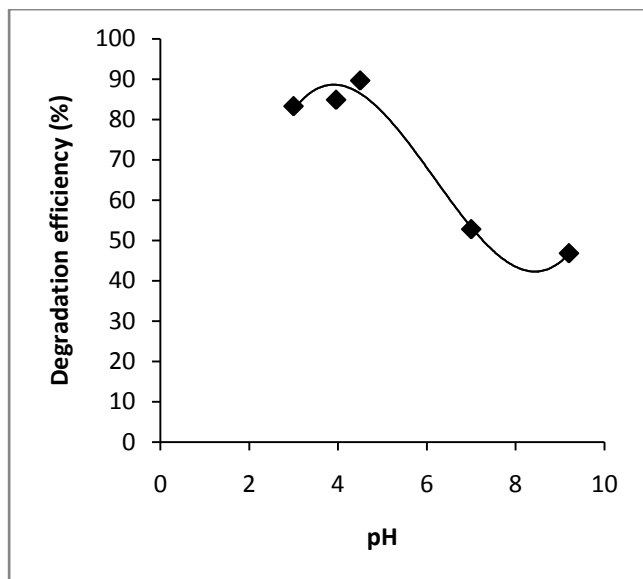


Fig.3. Effect of initial pH on degradation efficiency for 2- toluic acid (conditions: [2TA] =0.08mM, H_2O_2 /COD=5)

3.2 Effect of dose of H_2O_2 /COD ratio on degradation of 2- toluic acid

By carrying out a series of experiments of 2- toluic acid (with different ratio of H_2O_2 /COD namely 2, 3, 4, 5, 6); the optimum H_2O_2 stoichiometric ratio was found to be H_2O_2 /COD=5(Fig. 4).

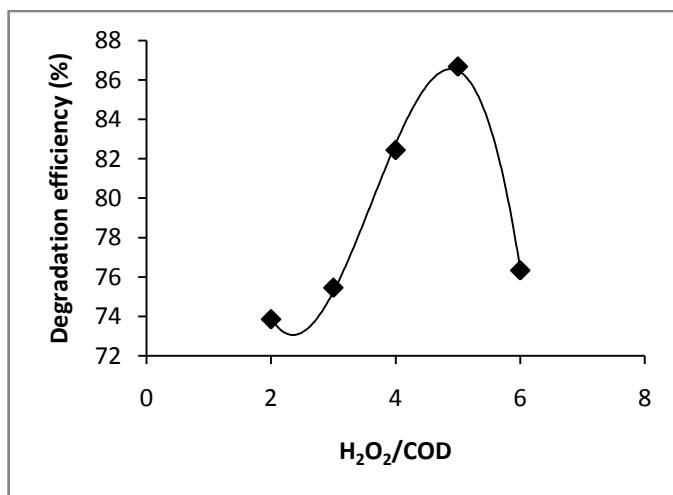


Fig. 4. Effect of initial H_2O_2 /COD on degradation efficiency for 2- toluic acid (conditions: [2TA]=0.08mM, pH=4.5)

3.3 Fenton process

3.3.1 Effect of initial H₂O₂ concentration on degradation of 2- toluic acid

Hydrogen peroxide plays the role of an oxidizing agent in Fenton process. The effect of change in H₂O₂ concentration on degradation efficiency for 2- toluic acid is depicted in Fig.5. The concentration of H₂O₂ was varied from 1 to 2 mM at room conditions while keeping the Fe²⁺ ion concentration at 9.3μM and pH at 3.0 ± 0.2. The degradation efficiency increases with increasing H₂O₂ concentration, due to incremental ·OH radical produced by UV enhanced H₂O₂. Maximum degradation efficiency was attained at 1.7mM. Further addition of H₂O₂, did not improve the degradation efficiency may be due to self decomposition of H₂O₂ to oxygen and water as in eq. (1). Moreover, the excess H₂O₂ react with ferric ions (Fe³⁺) to form weaker hydroperoxyl radical (HO₂·) as presented in eq.(3) and eq.(4),which is not as active as ·OH radical towards 2- toluic acid degradation.

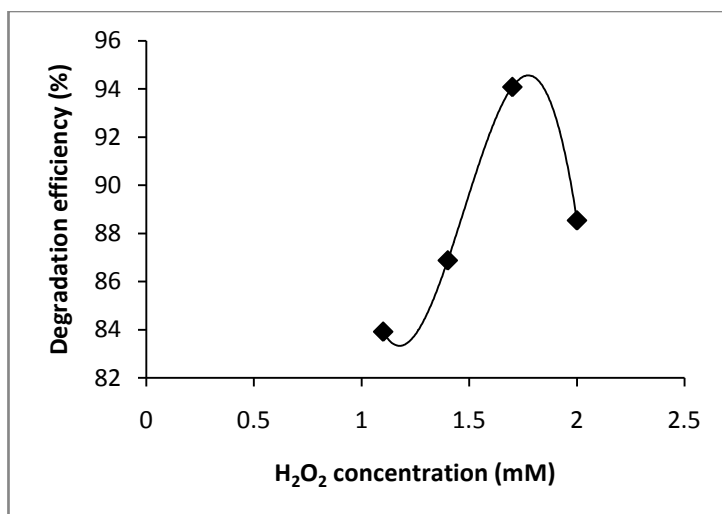
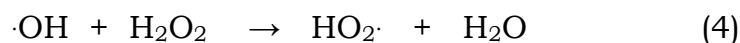
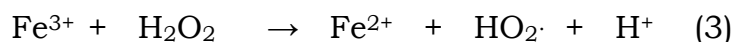
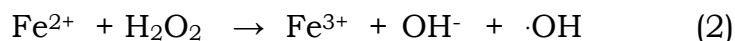


Fig. 5. Effect of initial H_2O_2 concentration on degradation of 2- toluic acid (conditions: $[\text{2TA}] = 0.08\text{mM}$, $\text{pH} = 3.0 \pm 0.2$, $[\text{Fe}^{2+}] = 9.3\mu\text{M}$).

To elucidate the role of Fe^{2+} ion on degradation of 2- toluic acid, a series of experiment were performed at room conditions by varying the concentration of Fe^{2+} ion from $3.2\mu\text{M}$ to $12\mu\text{M}$ for fixed H_2O_2 concentration of 1.7mM and at $\text{pH} 3.0 \pm 0.2$. The degradation efficiency for 2- toluic acid with various Fe^{2+} ion is illustrated in Fig 6. The degradation efficiency increased progressively with increase in Fe^{2+} ion concentration due to higher amount of $\cdot\text{OH}$ radical generated through eq.(1). Maximum degradation efficiency was achieved at $9.3\mu\text{M}$. Further increase in Fe^{2+} ion concentration did not correspondingly increase its reactivity probably due to direct reaction of $\cdot\text{OH}$ radical with metal ion (Joseph et al., 2000) as follows:

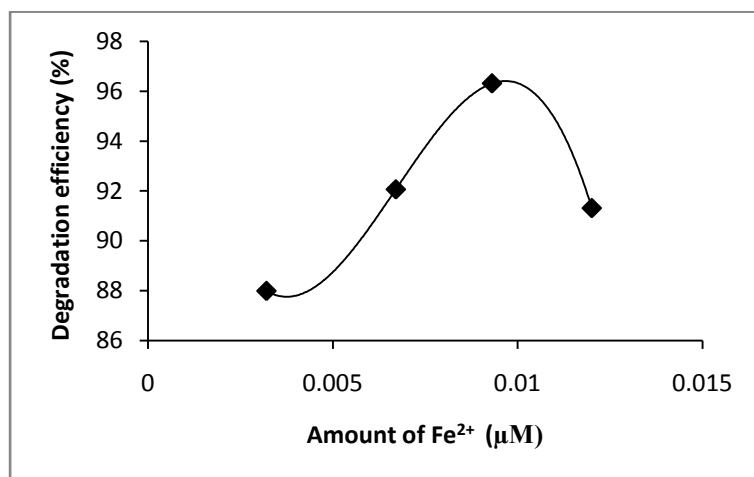


Fig. 6. Effect of initial Fe^{2+} concentration on degradation of 2- toluic acid (conditions: $[\text{2TA}] = 0.08\text{mM}$, $\text{pH} = 3.0 \pm 0.2$, $\text{H}_2\text{O}_2 = 1.7\text{mM}$).

4. Comparison of various AOPs studied and the kinetic studies

A comparison study was carried out for degradation of 2- toluic acid at optimum conditions for different AOPs studied like $\text{UV}/\text{H}_2\text{O}_2$ and $\text{UV}/\text{Fe}^{2+}/\text{H}_2\text{O}_2$ in terms of percentage degradation and rate constant is illustrated in Table 1

and Fig. 7 and was found that the rate of degradation is highest when a combination of UV radiation and hydrogen peroxide and iron catalyst was used.

The semilogarithmic graph of the concentration of 2- toluic acid with time yield a straight line indicating the reaction is of pseudo first order (eq. A).

$$-d/dt[c(X)] = kc(X) \quad (A)$$

Where $c(X)$ is the concentration of substrate and $k(\text{min}^{-1})$ is reaction rate constant.

Table1. Percentage degradation and rate constant values of photoperoxidation and photofenton processes

SNo	Process	Percentage degradation For first 40 min of process	$k(\text{min}^{-1})$
1	UV/H ₂ O ₂	51.58%	0.012
2	UV/Fe ²⁺ /H ₂ O ₂	96.31%	0.035

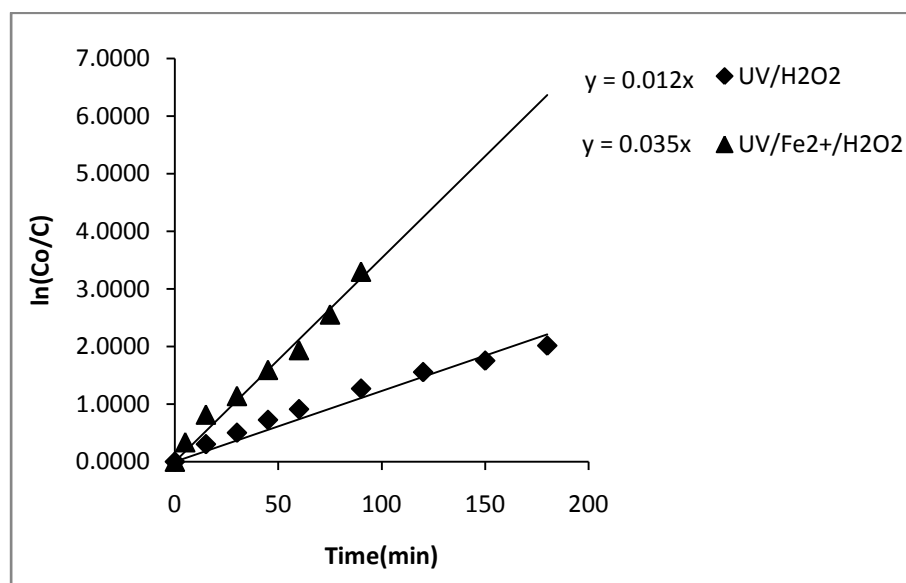
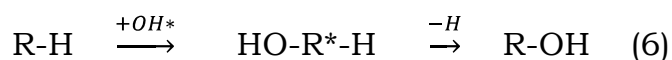


Fig 9. Comparative study of photoperoxidation and photofenton processes

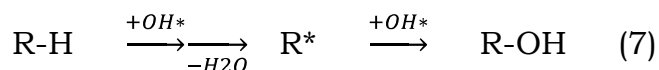
5. Reaction products

There are two possible mechanisms to explain hydroxylation (Omura & Matsuura, 1968):

1. The hydroxyl radical attacks the phenolic ring R forming a cyclohexadienyl radical (intermediate), which is converted by further abstraction of a hydrogen atom to the hydroxylated product as in eq. (6).



2. The hydroxyl radical abstracts a hydrogen atom from the phenolic compound R yielding a phenolic radical (intermediate). This in turn adds a hydroxyl radical giving the hydroxylated phenolic product as in eq (7).



6. Conclusions

Treatment of simulated wastewater containing 2- toluic acid by simple photoperoxidation and photofenton has been taken into consideration in the present study. On the basis of the results obtained the following conclusions have been made:

- The optimum operating conditions for photoperoxidation was $\text{H}_2\text{O}_2/\text{COD} = 5$ at an initial pH of 4.5 ± 0.2 . Under this condition the maximum degradation of 86.68% is achieved in 3 hrs.
- All the AOPs studied were modeled into pseudo-first-order kinetics, since peroxide in case of photoperoxidation ($\text{UV}/\text{H}_2\text{O}_2$) and peroxide and Fe^{2+} in case of photofenton are in excess concentration to the substrate.
- In the two AOPs studied the combination $\text{UV}/\text{Fe}^{2+}/\text{H}_2\text{O}_2$ was found to be the fastest among them. It took just 40 min to degrade 96.31% of the substrate.

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