Photodegradation of 2- Toluic Acid by Fenton Process

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Abstract: The present study was used to probe the treatment of simulated wastewater containing 2-toluic acid by photo-fenton processes. Experiments were conducted in a batch photoreactor to examine the effects of operating variables like concentration of Fe^{2+} and doses of H_2O_2. A pseudo-first order kinetic model was adopted to represent the photo-oxidative degradation of 2-toluic acid. The degradation of 2-toluic acid was found to be maximum at Fe^{2+} concentration of 0.0093mM/L and H_2O_2 concentration of 1.7mM/L.

Keywords: 2-toluic acid, photo-fenton processes, pseudo-first order.

Introduction:

Recent studies have demonstrated the presence of pharmaceuticals compounds in rivers, lakes and superficial freshwater 9[1-4]. 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(Legrini et. al.,1993; Kim et. al.,1997; Kim et. al.,1997). 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 (Kavitha et. al., 2005; Fernando et. al.,1992; Anipsitakis et. al., 2003; Beunrostro et. al., 2000; Gogate et. al., 2004; Bader et. al.,1981; Lin et. al.,1999).

2-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. 2-Toluic acid is produced as an industrial waste from olive oil distillation industries, chemical and pharmaceutical industries. The objective of this study is to degrade 2-toluic acid by photofenton process, to examine the effects of operating variables like dose of H_2O_2 and concentration of Fe^{2+} and to show that it follows a pseudo-first order kinetics.

Materials and methods

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 0.12 mM. Stock solution of H_2O_2 was prepared by diluting

30% w/v of peroxide (Qualigens) with distilled water. 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.

Experimental procedure: Batch experiments were conducted at room conditions to determine the H_2O_2 concentration and Fe^{2+} concentration during 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 0.12 mM 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 90min with H_2O_2 as oxidant.

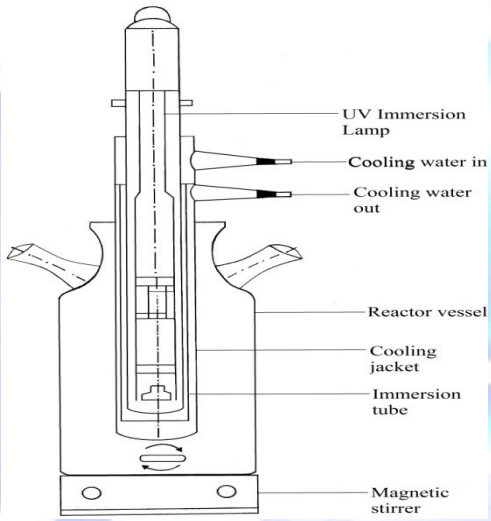

Fig. 1 Photoreactor

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 (Shimadzu UV 1800, UV Spectrophotometer) was used for this purpose. A calibration plot between absorbance and concentration of 2-toluic was plotted experimentally, which gave a high linear regression coefficient of 0.999 at 228nm (Fig. 2).

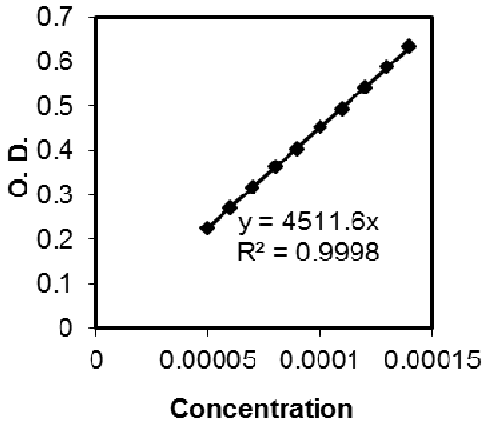

Fig. 2. Beer's law plot of 2-toluic acid

Results & Discussion

The results of the **photo-fenton process** in the present investigation are presented subsequently.

Effect of initial H_2O_2 concentration on degradation of 2-toluic acid:

Hydrogen peroxide plays the role of an oxidizing agent in Fenton process. The effect of change in H_2O_2 concentration on degradation efficiency for 2-toluic acid is depicted in Fig. 3. The concentration of H_2O_2 was varied from 1 to 2 mM at room conditions while keeping the Fe^{2+} ion concentration at 9.3µM and pH at 3.0 ± 0.2. The degradation efficiency increases with increasing H_2O_2 concentration, due to incremental ·OH radical produced by UV enhanced H_2O_2. Maximum degradation efficiency was attained at 1.7 mM. Further addition of H_2O_2, did not improve the degradation efficiency may be due to self decomposition of H_2O_2 to oxygen and water as in eq. (1). Moreover, the excess H_2O_2 react with ferric ions (Fe^{3+}) to form weaker hydroperoxyl radical (HO_2·) as presented in eq.(3) and eq.(4),which is not as active as ·OH radical towards 2-toluic acid degradation.

$$2H_2O_2 \rightarrow 2H_2O + O_2 \quad (1)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + \cdot OH \quad (2)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2\cdot + H^+ \quad (3)$$

$$\cdot OH + H_2O_2 \rightarrow HO_2\cdot + H_2O \quad (4)$$

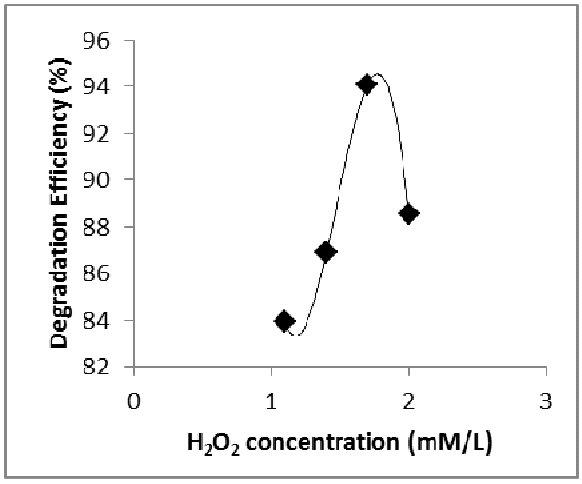

Fig. 3. Effect of initial H_2O_2 concentration on degradation of 2-toluic acid (conditions: [2TA] = 0.12mM, pH = 3.0 ± 0.2, [Fe^{2+}] = 9.3µM).

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 µM to 12 µM for fixed H_2O_2 concentration of 1.7 mM and at pH 3.0 ± 0.2. The degradation efficiency for 2-toluic acid at different Fe^{2+} ion concentration is illustrated in Fig 6. The degradation efficiency increased progressively with increase in Fe^{2+} ion concentration due to higher amount of ·OH radical generated as depicted in eq. (1). Maximum degradation efficiency was achieved at 9.3 µM. Further increase in Fe^{2+} ion concentration did not correspondingly increase its reactivity probably due to direct reaction of ·OH radical with metal ion (Joseph et al., 2000) as follows:

$$Fe^{2+} + {\cdot}OH \rightarrow Fe^{3+} + {}^{-}OH \qquad (5)$$

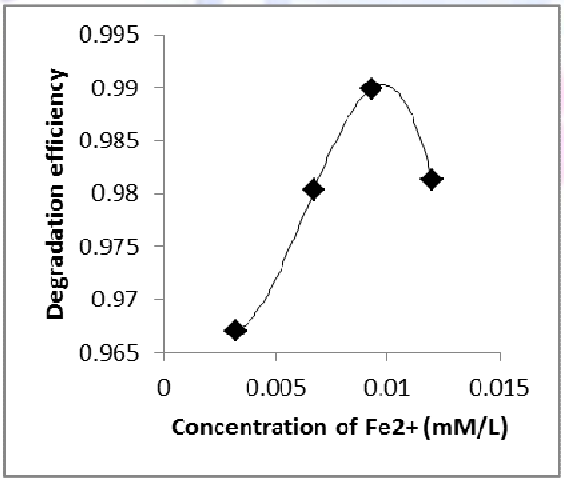

Fig. 4. Effect of initial Fe^{2+} concentration on degradation of 2-toluic acid (conditions: [2TA] = 0.12 mM, pH = 3.0 ± 0.2, H_2O_2 = 1.7mM).

The kinetic study

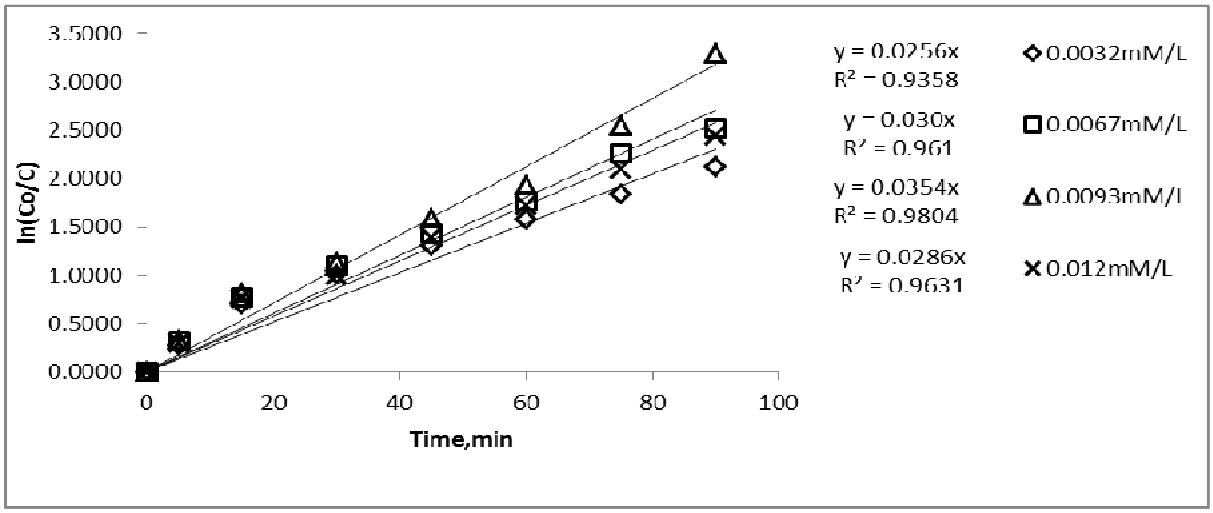

Fig. 5. Concentration decrease of 2- toluic acid as a function of time

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)

$-d[C(x)]/dt = k \cdot C(x)$ ..... (A)

Where C(x) is the concentration and k (min^{-1}) is reaction rate constant.

Conclusions

Treatment of simulated wastewater containing 2-toluic acid by photo-fenton process has been evaluated in the present study. The obtained results lead to following conclusions:

- The degradation of 2-toluic acid was found to be maximum at Fe^{2+} concentration of 0.0093mM/L and H_2O_2 concentration of 1.7mM/L.
- Under this condition the maximum degradation of 96% in 1.5 hrs. was obtained.
- The present AOP studied adhered to pseudo-first-order kinetics. This is justified since peroxide in case of photofenton ($UV/Fe^{2+}/H_2O_2$) is in excess as compared to the substrate concentration.

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