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# COMPARATIVE STUDY OF DEGRADATION OF 2-TOLUIC ACID BYPHOTOFENTON AND SOLAR FENTON PROCESSES

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**Abstract** :
Iron photochemical oxidation has been used to remove 2- Toluic acid present in cosmetic wastewater. Two different light systems were used: solar light and UV lamps. The effect of iron concentration and doses of $H_2O_2$ at pH 3 were investigated. At similar experimental conditions, the rate of degradation of 2- toluic acid for the different light systems were compared. The optimum conditions were found to be : pH 3, dose of 1.7 $mML^{-1}$ $H_2O_2$ and 0.0093 $mML^{-1}$ for Fe(II) and reaction time 90 min. The experimental results show that Fenton's oxidation process successfully achieved very good removal efficiency; over 96% when UV light is used and 80 % when solar light is used in 90 min reaction time.A pseudo-first order kinetic model was adopted to represent the photo-oxidative degradation of 2-toluic acid.
**Keywords:** 2- Toluic acid, photo- fenton process, photo-oxidative degradation.

## Introduction :

Advances in technology have resulted in greater water demands for industry. The volume of wastewater from the industries has increased, and needs treatment. Removal of organic contaminants from water present at low concentrations (ppm or below) requires the use of tertiary treatment methods for complete removal or high mineralization. Among these treatments, advanced oxidation processes (AOP) are usually selected for different reasons: economy, high efficiency, easy application, etc. (Beltran, 2004). Hydroxyl radical oxidation is the main common feature of these chemical processes (Glaze et al., 1987)[1-5].

Generally Fenton's oxidation process is pH adjustment, oxidation reaction reaction, neutralization and coagulation for precipitation. So, the organic substances are removed at two stages of the oxidation and the coagulation (Kange and Hwang, 2000). Solar photocatalytic degradation of the azo dye acid orange 24 by means of a photo Fenton reaction promoted by solar energy was used (Juan et al., 2006)[6-9]. 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. The process for manufacturing terephthalic acid generates liquid effluent streams that contain high levels of p-toluic acid, which is categorized as an environmentally hazardous material because of its toxicity and slow degradation.

In this present work, the effect of some variables (iron and hydrogen peroxide dose) and effect of solar radiation is compared with the radiation emitted by the UV lamps.

## 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 0.08 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. For photo Fenton and solar Fenton processes ferrous sulphateheptahydrate ($FeSO_4.7H_2O$) and hydrogen peroxide solution (30% w/w) were used are all of analytical grade obtained from Merck.Sodium hydroxide (1N) and sulphuric acid (1N) were used for pH adjustments.

### Methods

All experiments of photofenton processes conducted out in a photoreactor (Fig. 1) equipped with low pressure mercury lamp (8W, UV-C manufactured by Phillips, Holland) placed in its centre and the solar fenton reactions were carried out in open glass containers. During the reaction, the solution was stirred by magnetic pellet to ensure its homogeneity.Synthetic wastewater containing 0.08 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 90 min.

**Analyses**

The initial pH of the solution was measured using Elico pH meter LI-120 equipped with a combined calomel-glass electrode. The H2O2 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, ozone and H2O2 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).

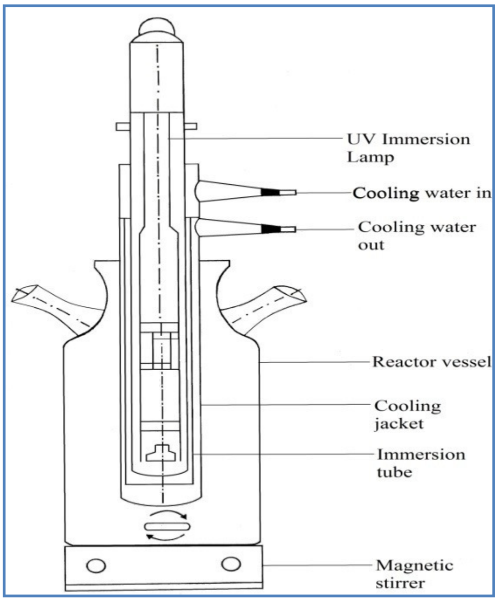


**Figure. 1**- Photoreactor

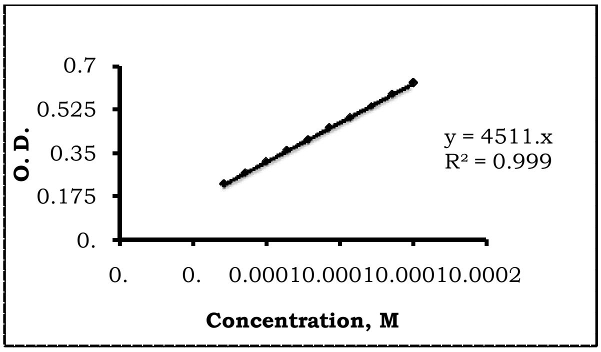


**Figure 2**. Beer's law plot of 2-toluic acid

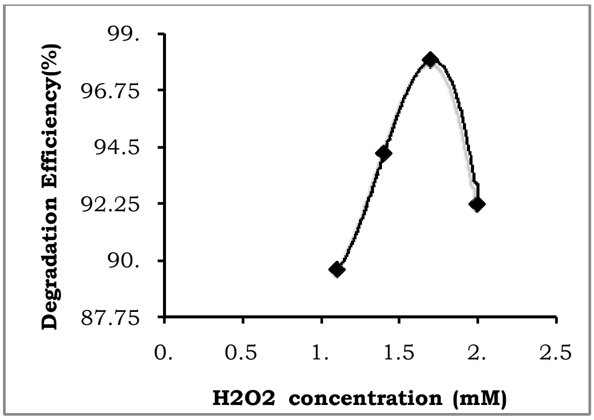


**Figure. 3.** Effect of initial $H_2O_2$ concentration on degradation of 2-toluic acid (conditions: [2TA] = 0.08mM, pH = 3.0 ± 0.2, [$Fe^{2+}$] = 9.3μM).

## Results and Discussion

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

**Photo-Fenton process**

- **Effect of initial $H_2O_2$ concentration**

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 ($HO_2\cdot$) as presented in eq.(3) and eq.(4),which is not as active as ·OH radical towards 2-toluic acid degradation.

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

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

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

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

- **Effect of $Fe^{2+}$ ion concentration**

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:

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

**Solar -Fentonprocess**

**In case of solar fenton processes, sunlight is used in place of UV lamp.**

- **Optimization of $Fe^{2+}$:**

$Fe^{2+}$ dose was varied from 0.0032 mM/L to 0.0012 mM/L at optimum $H_2O_2$ dose of evaluated earlier by photo-oxidation using $H_2O_2$ + UV combination. The pH of the solution was maintained between 3-3.1. The results for the optimisation of $Fe^{2+}$ concentration for 2-toluic acid solution are presented in Fig 5. Maximum degradation efficiency was achieved at 9.3 μM.

**Table1.** Summary of different AOP's studied

| S. No. | Process | Percentage degradation For one and a half hour of the process | k/(min$^{-1}$) |
|---|---|---|---|
| 1 | UV/$Fe^{2+}$/$H_2O_2$ | 96.31 | 0.0354 |
| 2 | Solar/$Fe^{2+}$/$H_2O_2$ | 80 | 0.0193 |

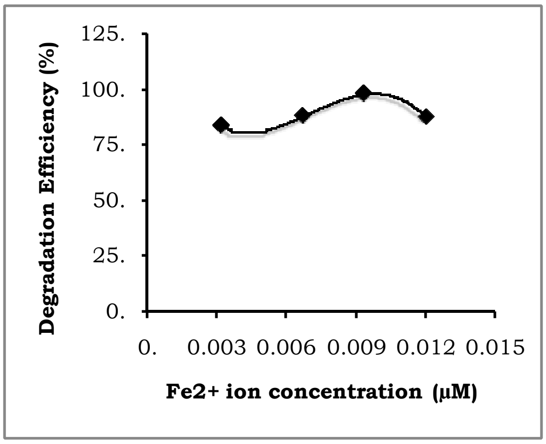


**Figure 4.** Effect of initial $Fe^{2+}$ concentration on degradation of 2-toluic acid (conditions: [2TA] = 0.08 mM, pH = 3.0 ± 0.2, $H_2O_2$ = 1.7mM).

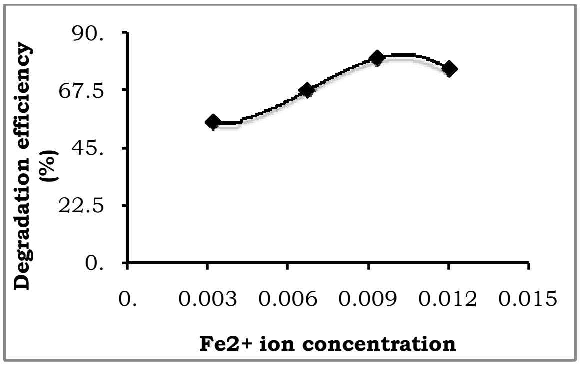


**Figure 5.** Effect of initial $Fe^{2+}$ concentration on degradation of 2-toluic acid in solar fenton process (conditions: [2TA] = 0.08 mM, pH = 3.0 ± 0.2, $H_2O_2$ = 1.7mM).

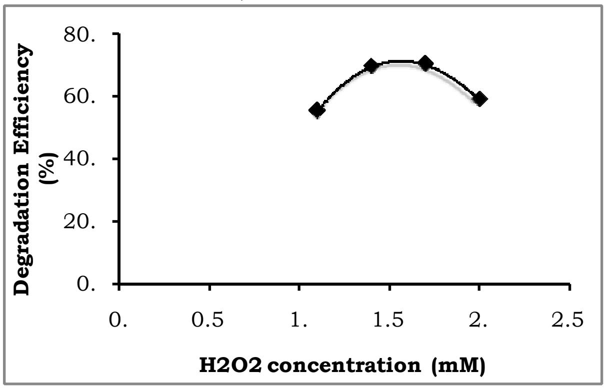


**Figure 6.** Effect of initial $H_2O_2$ concentration on degradation of 2-toluic acid in solar fenton process (conditions: [2TA] = 0.08mM, pH = 3.0 ± 0.2, [$Fe^{2+}$] = 9.3μM).

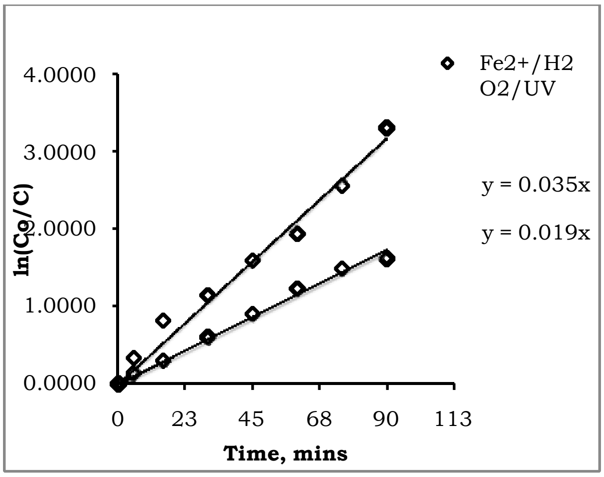


**Figure 7.** Concentration decrease of 2-toluic acid as a function of time by different AOP's studied.

- **Optimisation of $H_2O_2$ concentration**

The concentration of $H_2O_2$ for solar fenton processes 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. Maximum degradation efficiency was attained at 1.7 mM.

**Comparison of various AOPs studied and the kinetic studies**

A comparative study was carried out for degradation of 2-toluic acid at optimum conditions for different AOPs studied like $UV/Fe^{2+}/H_2O_2$ and $Solar/Fe^{2+}/H_2O_2$ in terms of percentage degradation and rate constant is illustrated in Table 1 and was found that the rate of degradation is highest when a combination of UV radiation, $Fe^{2+}$ ion concentration and hydrogen peroxide was used (Fig. 8).

The semilogarithmicgraph of the concentration of 2-toluic acid with time yield a straight line indicating the reaction is of pseudofirst order (eq. A)

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

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

## Conclusions

The following conclusions might be drawn as a result of application of photo- Fenton /solar-Fenton processes which indicate that

- The optimum operating conditions for photo-Fenton process of treated water was 9.3μM $Fe^{2+}$ ion concentration 1.7 mM $H_2O_2$ concentration initial pH of 3.0±0.2. Under this condition the maximum degradation of 96% in 1.5 hrs. was obtained.
- All the AOPs studied adhered to pseudo-first-order kinetics. This is justified since peroxide and $Fe^{2+}$ in case of photo-fenton are in excess as compared to the substrate concentration.
- The use of Fe(II)/UV or Fe(III)/solar light oxidation systems is a promising technology to reduce 2- toluic acid concentration from water.

## Acknowledgement

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