



## DEGRADATION OF SALICYLIC ACID BY UV, UV/ H<sub>2</sub>O<sub>2</sub>, UV/O<sub>3</sub>, PHOTOFENTON PROCESSES

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### ABSTRACT

The present study was used to probe the treatment of simulated wastewater containing salicylic acid by UV, UV/ H<sub>2</sub>O<sub>2</sub>, UV/O<sub>3</sub>, photofenton processes. Experiments were conducted in a batch photoreactor to examine the effects of operating variables like pH, ratio of H<sub>2</sub>O<sub>2</sub>/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 salicylic acid. The degradation rate of salicylic acid obeys the following sequence: photoperoxone(O<sub>3</sub>/UV/ H<sub>2</sub>O<sub>2</sub>) > photofenton(UV/Fe<sup>2+</sup>/ H<sub>2</sub>O<sub>2</sub>)>photoperoxidation(UV/ H<sub>2</sub>O<sub>2</sub>) > photolysis(UV).

**Keywords:** Salicylic acid, photoperoxone, photoperoxidation, photofenton, photolysis.

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### 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).

Salicylic acid is produced as an industrial waste from olive oil distillation industries, chemical and pharmaceutical industries. Decomposition of organic substances by ozonation is one of the most promising processes in water and wastewater treatments. Ozonation is used for the removal of odorous compounds, hazardous chemicals like pesticides and chlorinated organic compounds (11, 12). In Fenton processes; 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 salicylic acid by various AOP's (UV/ H<sub>2</sub>O<sub>2</sub>, UV/O<sub>3</sub>, and UV/Fe<sup>2+</sup>/ H<sub>2</sub>O<sub>2</sub>) and compare their degradation rates and to show that it follows a pseudo-first order kinetics.

### EXPERIMENTAL

#### Chemicals

Analytical grade salicylic acid was purchased from Merck, India; and was used as received without any further purification and stock solution of 0.01M of salicylic acid was prepared. Initial concentration of salicylic acid used during the experimental runs was 0.08 mM. Stock solution of H<sub>2</sub>O<sub>2</sub> was prepared by diluting 30% w/v of peroxide (Qualigens) with distilled water. Analytical grade ferrous sulphate heptahydrate (FeSO<sub>4</sub>.7H<sub>2</sub>O, 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. Oxygen cylinders were used for ozone generation.

### Procedure

Batch experiments were conducted at room conditions to determine the effect of pH,  $H_2O_2$  concentration,  $Fe^{2+}$  ion concentration and ozone concentration with different combinations during degradation of salicylic 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. Ozone was produced using an ozone generator, which is a high frequency cold plasma / cold corona ozone generator. The generator was fed with an inlet of pure and dried oxygen gas from an oxygen cylinder with an oxygen flow meter.

Synthetic wastewater containing 0.08 mM solution of salicylic 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 3 h with  $H_2O_2$  as oxidant; 1.5 h when Fenton reagent was used and 45 min when  $O_3$  was used as oxidant.

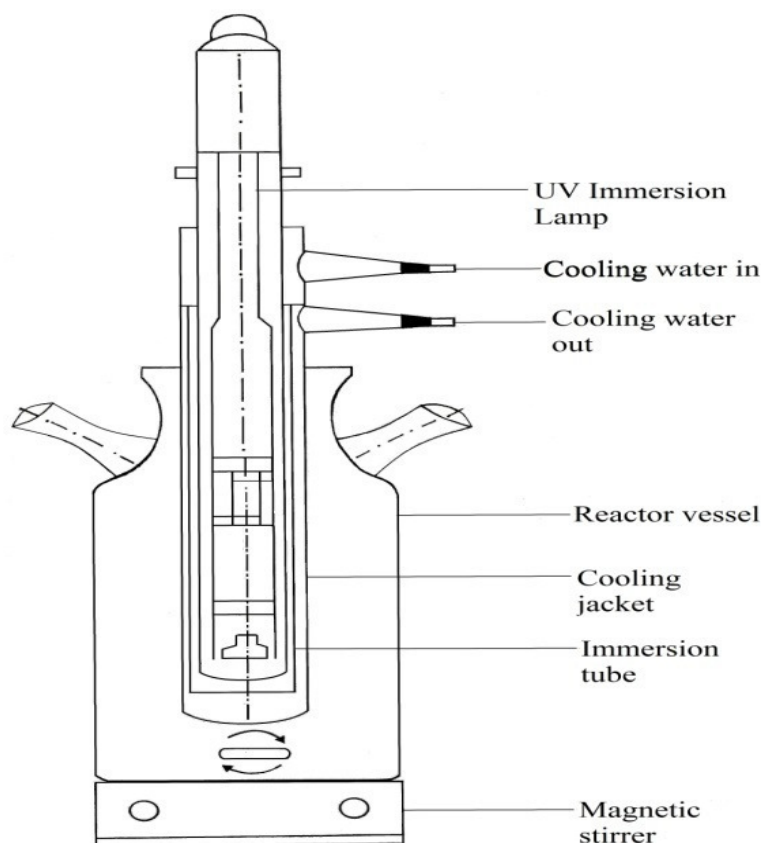


Fig.-1 :Photoreactor

### 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 salicylic acid, ozone 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 salicylic acid was plotted experimentally, which gave a high linear regression coefficient of 0.997 at 229.4nm (Fig. 2).

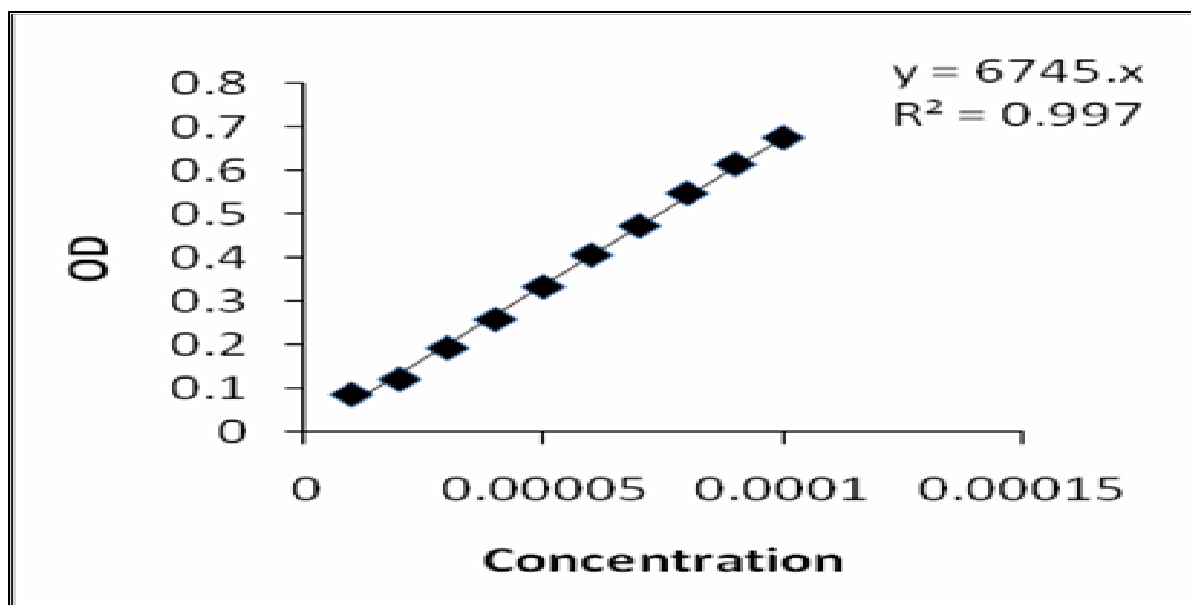


Fig. -2: Beer's law plot of salicylic acid

## RESULTS & DISCUSSION

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

### Effect of pH

pH is one of the most important parameters to be studied. The rate of degradation of salicylic 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 salicylic acid was achieved at neutral pH 7 and shows decreasing trend of degradation at higher and lower pH.

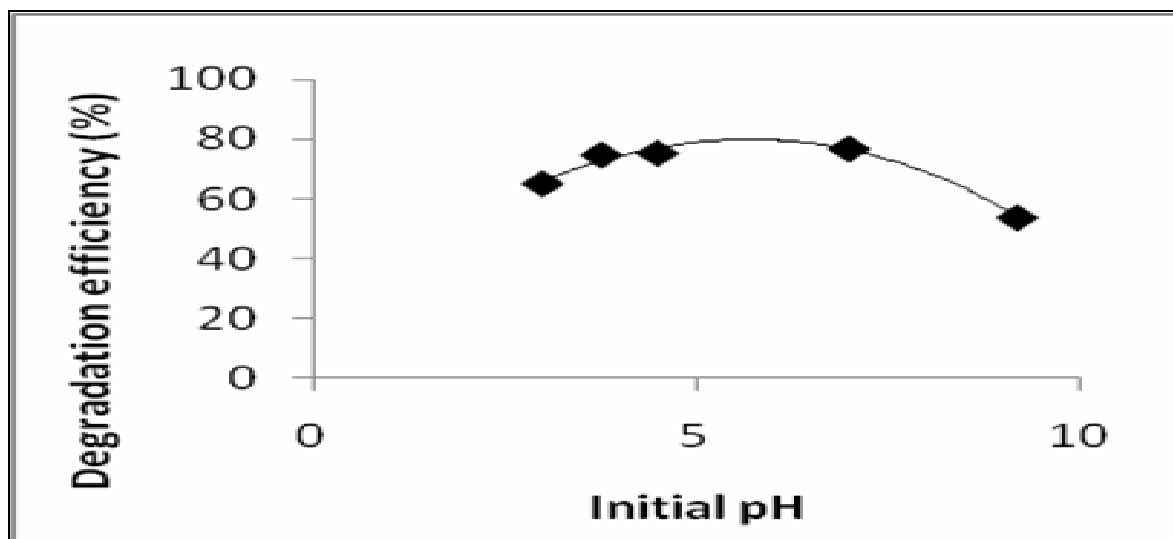


Fig.-3: Effect of initial pH on degradation efficiency for salicylic acid  
(conditions: [SA] = 0.08 mM,  $H_2O_2$  /COD = 5)

### Effect of dose of H<sub>2</sub>O<sub>2</sub>/COD ratio on degradation of salicylic acid

By carrying out a series of experiments of salicylic acid (with different ratio of H<sub>2</sub>O<sub>2</sub>/COD namely 2, 3, 4, 5, 6); the optimum H<sub>2</sub>O<sub>2</sub> stoichiometric ratio was found to be H<sub>2</sub>O<sub>2</sub>/COD=5(Fig. 4).

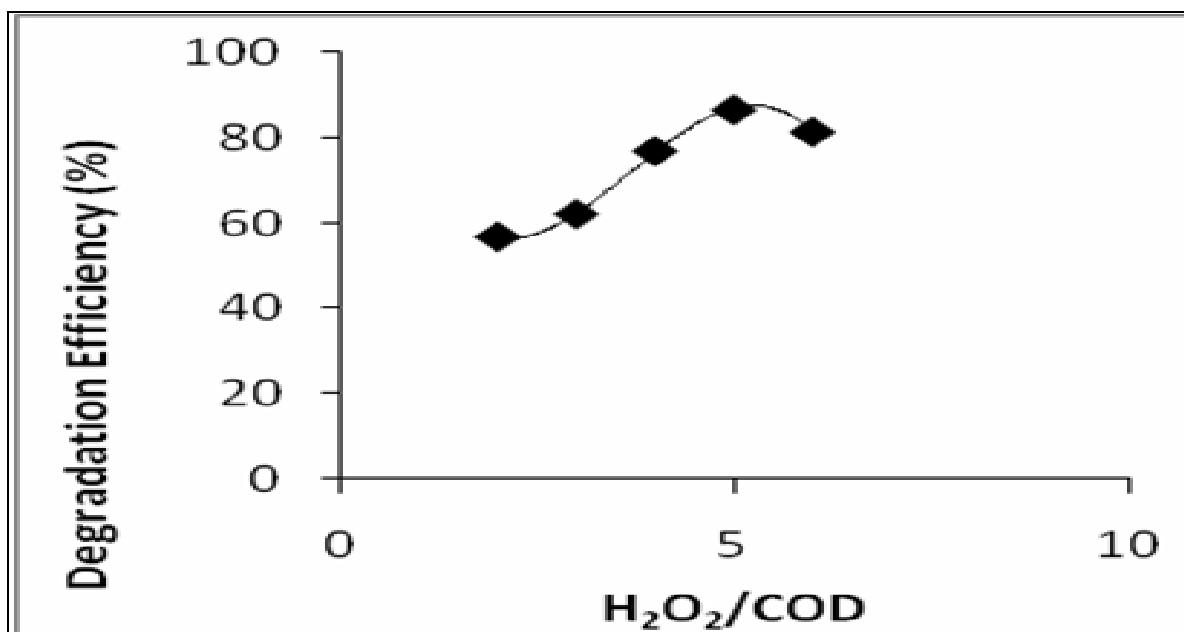
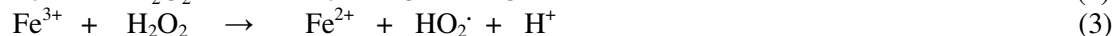


Fig.-4: Effect of initial H<sub>2</sub>O<sub>2</sub>/COD on degradation efficiency for salicylic acid (conditions: [SA] = 0.08 mM, pH = 7)

### Fenton process

#### Effect of initial H<sub>2</sub>O<sub>2</sub> concentration on degradation of salicylic acid

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



To elucidate the role of Fe<sup>2+</sup> ion on degradation of salicylic acid, a series of experiment were performed at room conditions by varying the concentration of Fe<sup>2+</sup> ion from 3.2 μM to 12 μM for fixed H<sub>2</sub>O<sub>2</sub> concentration of 1.7 mM and at pH 3.0 ± 0.2. The degradation efficiency for salicylic acid at different Fe<sup>2+</sup> ion concentration is illustrated in Fig 6. The degradation efficiency increased progressively with increase in Fe<sup>2+</sup> 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<sup>2+</sup> 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:



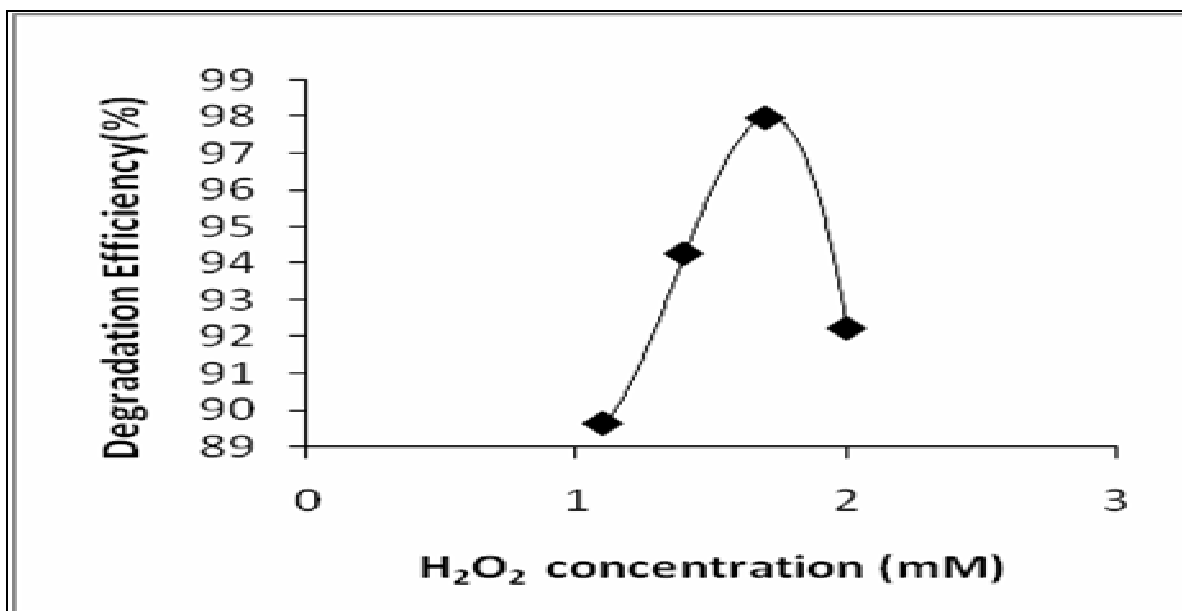


Fig.-5: Effect of initial H<sub>2</sub>O<sub>2</sub> concentration on degradation of salicylic acid (conditions: [SA] = 0.08mM, pH = 3.0 ± 0.2, [Fe<sup>2+</sup>] = 9.3μM).

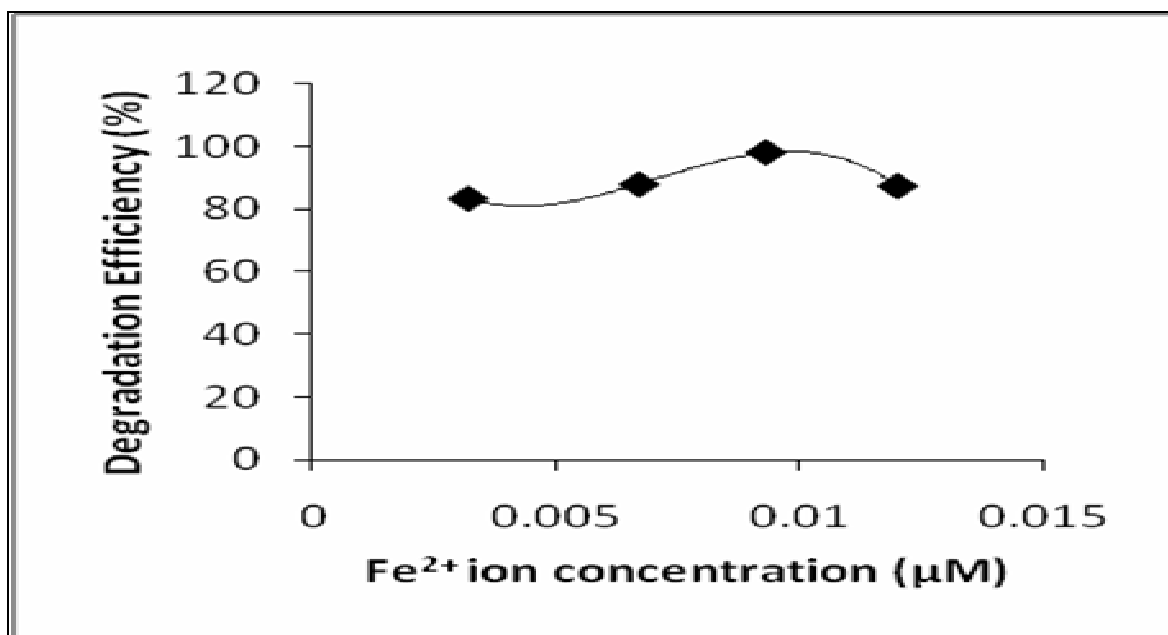


Fig.-6: Effect of initial Fe<sup>2+</sup> concentration on degradation of salicylic acid (conditions: [SA] = 0.08 mM, pH = 3.0 ± 0.2, H<sub>2</sub>O<sub>2</sub> = 1.7mM).

#### Effect of ozone at different combinations with UV and H<sub>2</sub>O<sub>2</sub> on degradation of salicylic acid

To elucidate the role of ozone on degradation of salicylic acid, a series of experiments were performed at room conditions and optimum pH by varying the conditions as follows:

1. Only O<sub>3</sub>

2. H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub>
3. UV/O<sub>3</sub>
4. UV/O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>

The degradation of salicylic acid for these various conditions is illustrated in Fig. 7. In photoperoxone(UV/O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>) the rate of formation of hydroxyl radicals are significantly enhanced due to UV irradiation and hence there is significant increase in the in the rates of ozonation in the presence of hydrogen peroxide and UV (13-16). Thus it can be said that the overall efficiency of the degradation process will be significantly enhanced when a combination of UV radiation, ozone and hydrogen peroxide was used. The addition of H<sub>2</sub>O<sub>2</sub> increases the contribution of ·OH radicals and helps in reducing the cost of oxidant addition, as it reduces the amount of ozone necessary to completely mineralize a pollutant or to produce a readily biodegradable wastewater solution of initially poorly biodegradable mixtures.

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

A comparative study was carried out for degradation of salicylic acid at optimum conditions for different AOPs studied like UV/H<sub>2</sub>O<sub>2</sub>; UV/Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub>; O<sub>3</sub>; O<sub>3</sub>/UV; O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>; O<sub>3</sub>/UV/H<sub>2</sub>O<sub>2</sub> 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, ozone and hydrogen peroxide was used (Fig. 8).

The semilogarithmic graph of the concentration of salicylic acid with time yield a straight line indicating the reaction is of pseudo first order , as-

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

Where C(x) is the concentration and k (min<sup>-1</sup>) is reaction rate constant.

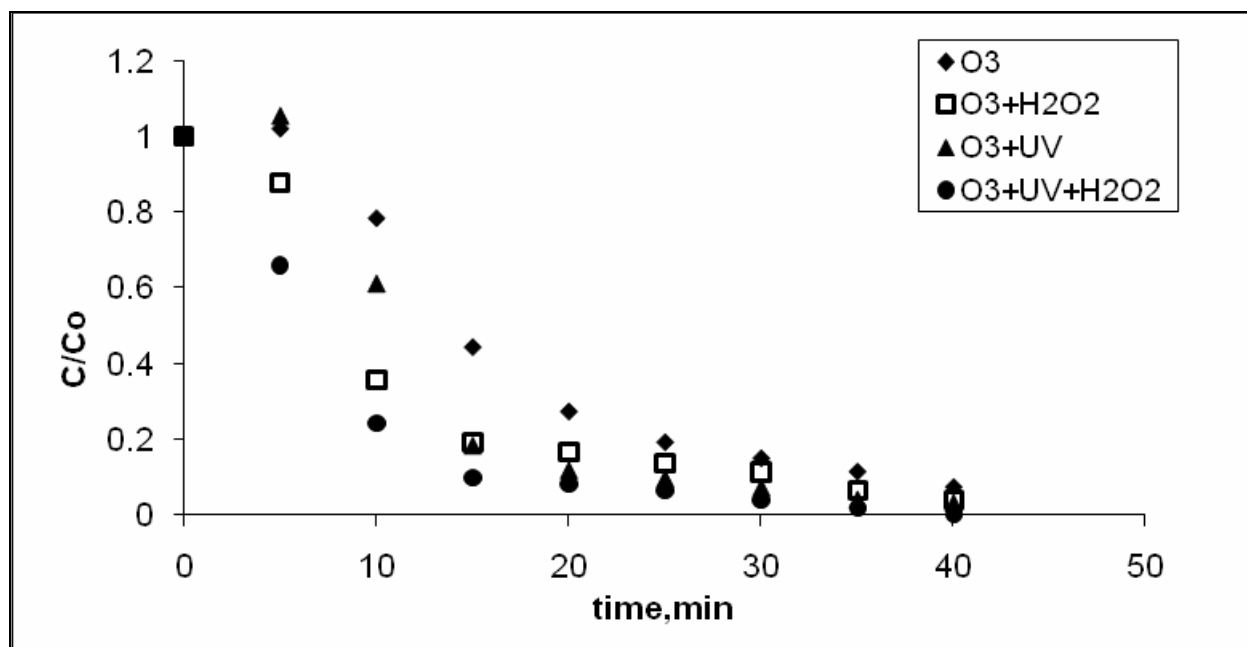


Fig.-7: Degradation of salicylic acid by ozonation in different combinations.

### CONCLUSIONS

Treatment of simulated wastewater containing salicylic acid by simple photoperoxidation, photofenton and photoperoxone has been evaluated in the present study. The obtained results lead to following conclusions:

1. The optimum operating conditions for photoperoxidation of treated water was  $H_2O_2/COD = 5$  at an initial pH of  $7.0 \pm 0.2$ . Under this condition the maximum degradation of 87% in 3 hrs. was obtained.
2. All the AOPs studied adhered to pseudo-first-order kinetics. This is justified since peroxide in case of photoperoxidation (UV/ $H_2O_2$ ); ozone and peroxide in case of photoperoxone (UV/ $H_2O_2/O_3$ ) and peroxide and  $Fe^{2+}$  in case of photofenton are in excess as compared to the substrate concentration .
3. Among all the AOPs studied in this investigation, the combination UV/ $O_3/H_2O_2$  was found to be the fastest and it took just 40 min to degrade 99.6% of the substrate.

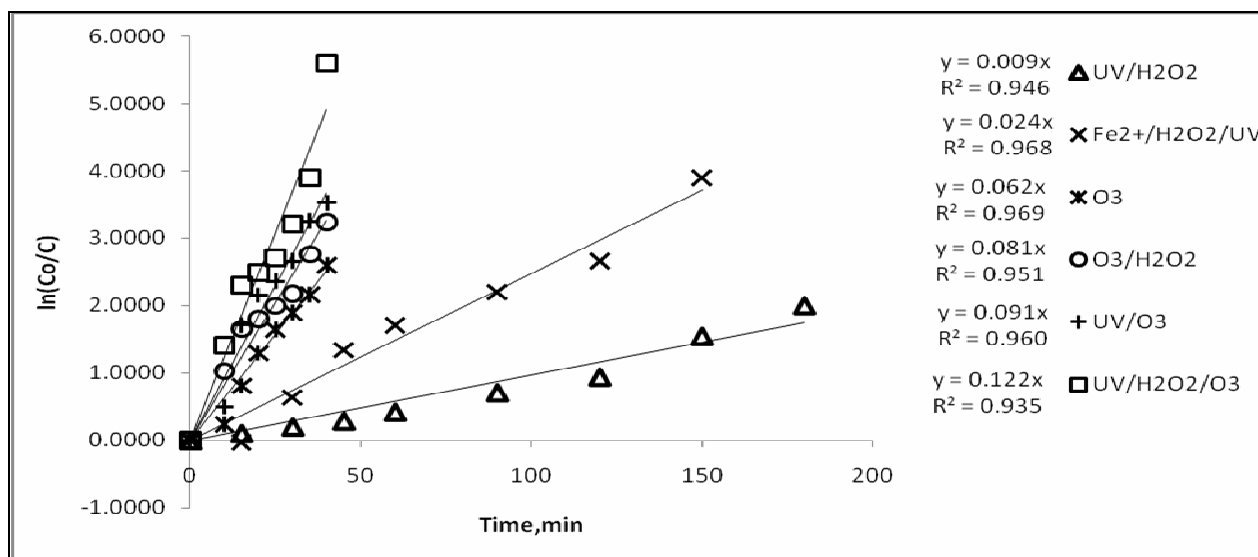


Fig.-8: Concentration decrease of salicylic acid as a function of time by different AOP's studied.

Table-1: Summary of different AOP's studied

S.No.	Process	Percentage degradation for first hour of process	k/(min <sup>-1</sup> )
1	UV/ $H_2O_2$	25.19	0.009
2	UV/ $Fe^{2+}/H_2O_2$	81.85	0.024
3	$O_3$	92.59	0.062
4	$O_3/H_2O_2$	96.11	0.081
5	$O_3/UV$	97.04	0.091
6	$O_3/H_2O_2/UV$	99.63	0.122

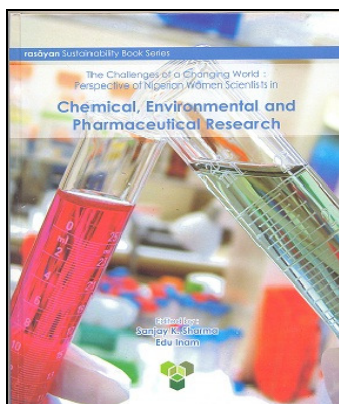
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