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Short Communication

KINETIC STUDIES OF DEGRADATION OF BENZOIC ACID AND SALICYLIC ACID THROUGH OZONATION, PEROXONE, PHOTOOZONATION AND PHOTOPEROXONE

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ABSTRACT

In this study, benzoic acid and salicylic acid in their aqueous solutions were treated by ozonation, photo-ozonation, photoperoxone and photoperoxone processes. A batch photoreactor with 8W low pressure mercury vapour lamp was used to carry out the experiments for examining the effects of various combinations of ozone, H_2O_2 and UV and their rates of degradation were compared. The concentration of the substrate was determined with an UV-visible spectrophotometer. The photodegradation processes conformed to first-order kinetics. The degradation rate of the two substrates is as follows: photoperoxone ($UV/O_3/H_2O_2$)> photoozonation(UV/O_3)> peroxone(O_3/H_2O_2)> ozonation(O_3).

Keywords: Benzoic acid, Salicylic acid, Ozonation, Photo-ozonation, Peroxone, Photoperoxone.

1. INTRODUCTION

Over the past several years, various studies have reported the presence of a large number of pharmaceuticals in surface waters, and also in groundwater. Surface water and groundwater are widely used as potable water resources. The widespread presence of pharmaceutical products can therefore have an adverse impact on the purity of drinking water. The complete elimination or reduction of harmful organic pollutants in wastewater to an acceptable level prescribed by environmental protection agencies is of paramount importance in wastewater treatment. Advanced oxidation processes (AOPs) are the most promising technologies for the destruction of harmful organic contaminants [1-3]. Therefore, AOPs are of great interest to the scientific and industry communities involved in water treatment and were successfully applied to the detox of water polluted by a wide variety of chemicals such as pesticides, phenols, hydrocarbons, surfactants, dyes and pharmaceutical waste [4-10].

In industries like toothpastes, preservatives, cosmetics, mouthwash, pharmaceuticals and artificial flavours; benzoic acid is produced as an industry waste. And salicylic acid is an industrial waste produced from pharmaceutical, chemical and olive oil distilleries. Ozonation is a promising technique in wastewater treatments for degradation of organic pollutants. Ozonation is used to eliminate odorants, harmful chemicals such as pesticides and chlorinated organic compounds [11, 12].

This study aims at the degradation of benzoic acid and salicylic acid by different AOP's (O_3, O_3/ H_2O_2, UV/O_3, and UV/O_3/ H_2O_2) and compare the rate of degradation and demonstrate that it follows a pseudo-first order kinetics.

2. EXPERIMENTAL

2.1. Chemicals

Benzoic acid (analytical grade, Merck, India) and salicylic acid (analytical grade, Merck, India) were used to prepare stock solution of 0.01M. Initial concentration of 0.08mM was used during the experimental runs. H_2O_2 stock solution was prepared by diluting 30% w/v of hydrogen peroxide (Qualigens) with distilled water. Light-tolerant amber Pyrex glass bottles were used to store the stock solutions. For ozone generation, Oxygen cylinders were used.

2.2. Experimental procedure

Batch experiments were carried out under environmental conditions to determine the effect of ozone concentration with various combinations during substrate degradation. A photoreactor (Fig. 1) fitted with low pressure mercury lamp (8W, UV-C manufactured by Phillips, Holland) placed in its centre was used to carry out the experiments. To ensure homogeneous mixing of the solution, magnetic stirrer was used. A high frequency cold plasma/cold corona ozone generator was used to produce ozone which was supplied by an inlet of pure, dried oxygen gas from an oxygen cylinder equipped with an oxygen flowmeter.

In this study, 0.08mM synthetic wastewater solution of benzoic acid prepared in double distilled water was used. 750 ml. of this solution was taken in the photoreactor, irradiated with an 8W UV lamp. Various experiments were conducted using UV light with different oxidant combinations. A general degradation reaction was conducted for 45 minutes.

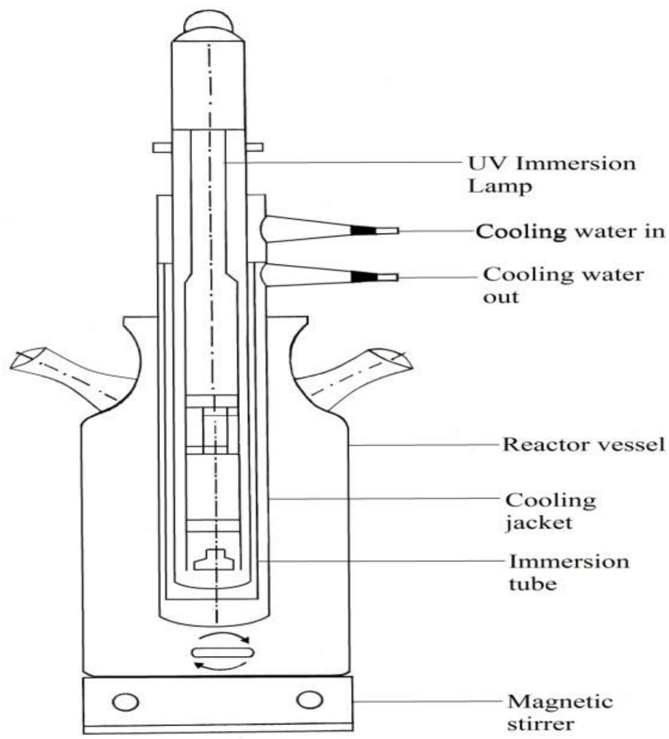

Fig. 1: Photoreactor

2.3. Analyses

An Elico pH meter (LI-120) equipped with a combined calomel-glass electrode was used to measure the initial pH of the solution. The H_2O_2 concentration was determined using standard iodometric titration method described in Jeffery et al. (1989) [13]. The concentration of benzoic acid, ozone and H_2O_2 was determined by UV-visible spectrophotometric method. A UV-visible spectrophotometer (Spectrascan UV 2600, Chemito, India) was used in this study. Calibration plots were plotted between absorbance and concentration experimentally, giving a high linear regression coefficient of 0.999 at 228 nm for benzoic acid (Fig. 2) and 0.997 at 229.4nm for salicylic acid (Fig. 3)

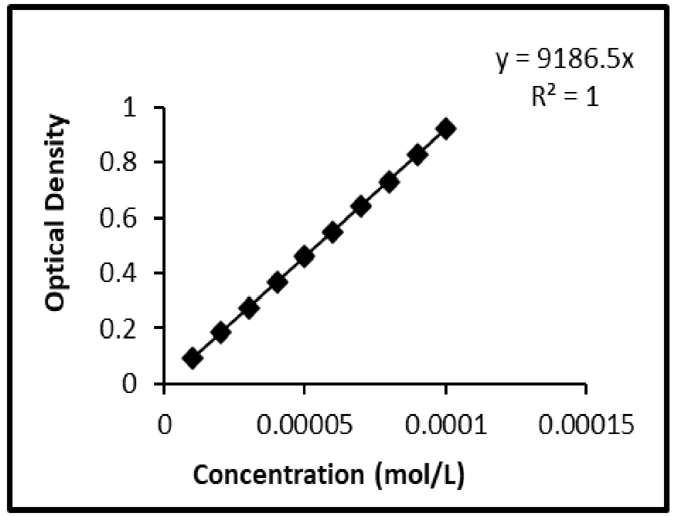

Fig. 2: Calibration plot of benzoic acid

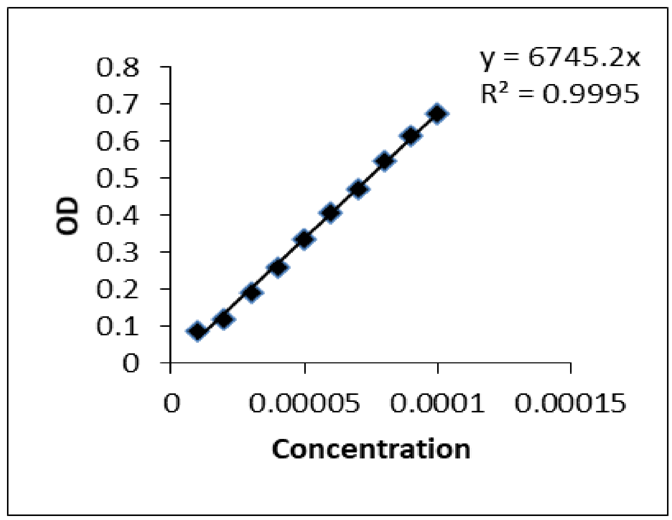

Fig. 3: Calibration plot of salicylic acid

3. RESULTS AND DISCUSSION

3.1. Effect of ozone at different combinations with UV and H_2O_2 on degradation of benzoic acid and salicylic acid

A series of experiments were carried out to elucidate the role of ozone on the degradation of both substrates under ambient conditions and at an optimum pH by varying the conditions as follows:

i. Only O_3 (Ozonation)
ii. H_2O_2 / O_3 (Peroxone)
iii. UV/O_3 (Photo-ozonation)
iv. UV/O_3/H_2O_2 (Photo-peroxone)

The degradation pattern of benzoic acid and salicylic acid for the above-mentioned conditions are illustrated in fig. 4 and fig. 5 respectively. The first step is ozone decay, accelerated by initiators HO^- ions, to form secondary oxidants such as $HO^{\bullet}$ radicals, which react non-selectively and immediately with pollutants. The AOP with UV radiation and ozone is initiated by the photolysis of ozone. The photodecomposition of ozone causes formation of two hydroxyl radicals, which do recombine producing hydrogen peroxide:

$$H_2O + O_3 + h\upsilon \rightarrow 2\,HO^{\bullet} + O_2 \quad (1)$$

$$2\,HO^{\bullet} \rightarrow H_2O_2 \quad (2)$$

The hydrogen peroxide thus generated, combine with ozone resulting in an increased hydroxyl radical concentration is explained as peroxone process. H_2O_2 in aqueous solution is partially dissociated as the hydro-peroxide anion (HO_2^{-}), which reacts with ozone, decomposing this and giving rise to a series of chain reactions with the participation of hydroxyl radicals. In the global reaction two ozone molecules produce two hydroxyl radicals [eq. 3].

$$H_2O_2 + 2O_3 \rightarrow 2HO^{\cdot} + 3O_2 \quad (3)$$

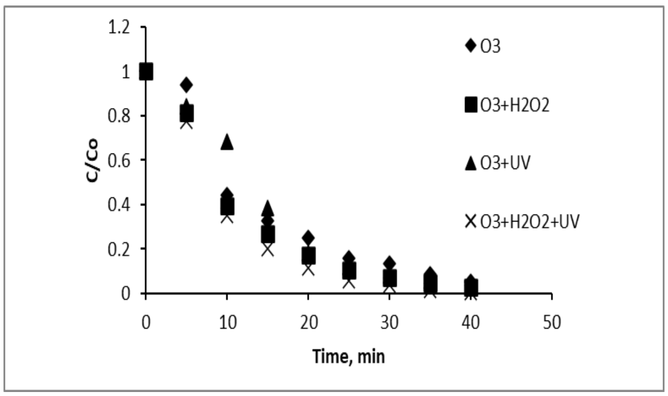

Fig. 4: Degradation of benzoic acid by different ozonation combinations.

The reaction mechanism of photo-peroxone is a combination of the binary systems photo-ozonation, UV/O_3 and peroxone, O_3/H_2O_2, leading to the generation of $HO^{\cdot}$ radicals. In photoperoxone ($UV/O_3/H_2O_2$), the rate of formation of hydroxyl radicals are significantly enhanced due to UV irradiation and hence there is significant increase in the rates of ozonation in the presence of hydrogen peroxide and UV.

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_2O_2 increases the contribution of $^{\cdot}OH$ 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.

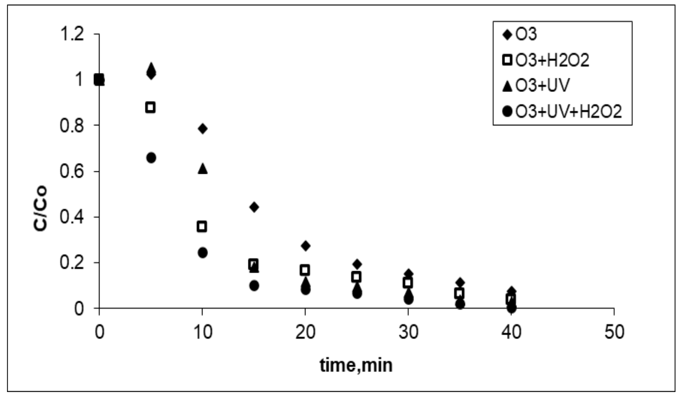

Fig. 5: Degradation of salicylic acid bydifferent ozonation combinations.

3.2. Comparison of various AOPs studied and the kinetic studies

A comparison was made in the study of degradation kinetics of benzoic acid and salicylic acid for the different AOPs studied like O_3; O_3/UV; O_3/H_2O_2; $O_3/UV/H_2O_2$ at optimum conditions in terms of percentage decay and rate constant as described in table 1 and has been found to have the highest rate of decay
when a combination of UV radiation, ozone and
hydrogen peroxide has been used.

The semi-logarithmic graph of the concentration of benzoic acid and salicylic acid over time gives a straight line showing that the reaction is pseudo-first order (eq.4).

$$-d[c(X)]/dt = kc(X) \quad (4)$$

where, c(X) = concentration of substrate,
k(min^{-1}) = reaction rate constant.

Table 1: Comparison of degradation kinetics

S. No	Process	Percentage degradation For first 40 min min of process		k(min^{-1})	
		Benzoic acid	Salicylic acid	Benzoic acid	Salicylic acid
1	O_3	94.83	92.59	0.071	0.062
2	O_3/H_2O_2	96.73	97.04	0.082	0.091
3	O_3/UV	97.42	96.11	0.088	0.081
4	$O_3/H_2O_2/UV$	99.72	99.63	0.124	0.122

3.2.1. *Reaction products*

To explain hydroxylation, Omura & Matsuura in 1968 [14], had explained two possible mechanisms:

1. The phenolic ring R is attacked by the hydroxyl radical by forming a cyclohexadienyl (intermediate) radical, which is further converted by the subsequent abstraction of a hydrogen atom to the hydroxylated product. as in eq. (5).

$$\text{R-H} \xrightarrow{+OH*} \text{HO-R*-H} \xrightarrow{-H} \text{R-OH} \quad (5)$$

2. A hydrogen atom is abstracted by the hydroxyl radical from the phenolic compound R, which yields a phenolic radical (intermediate). This further adds a hydroxyl radical giving the hydroxylated phenolic product as in eq (6).

$$\text{R-H} \xrightarrow[-H2O]{+OH*} \text{R*} \xrightarrow{+OH*} \text{R-OH} \quad (6)$$

4. CONCLUSION

In this study, simulated wastewater containing benzoic acid or salicylic acid was treated by simple ozonation, photo-ozonation, peroxone and photoperoxone processes. The results obtained enabled the following conclusions to be drawn:

- Since the oxidants ozone and or peroxide in all the cases are in excess concentration to the substrate, all AOPs investigated were modelled in pseudo-first order kinetics.
- In all of the AOPs investigated, the $UV/O_3/H_2O_2$ combination was the fastest. The decay of 99.72% benzoic acid and 99.63% salicylic acid took only 40 minutes.
- The degradation rate of benzoic acid was found to be greater as compared to salicylic acid because -OH is an electron donor group and the ring will be stabilised by resonance in a case of salicylic acid.

Conflict of interest

None declared

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