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A study on the enhancement of sonochemical degradation of eosin B using other advanced oxidation processes

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ABSTRACT

Eosin B is a xanthenes dye and is a derivate of fluorescein. The efficacy of sonochemical degradation coupled with other advanced oxidation process (AOP's) has been studied for eosin B degradation in aqueous solution. The study compares the effects of H_2O_2 concentration, saturating gas (argon, N_2, and O_2), temperature and pH (3–11). Furthermore, kinetic comparison and a figure of merit for the electrical energy consumption were carried out for the degradation under combination of different AOP's. Higher rate constant was obtained under Ar as a saturating gas and higher mineralization rate was found under acidic condition. It was also observed that rate constant decreases with the increase in temperature. The kinetic analysis indicate that of all the degrading setups used, the $US + O_3$ was fastest in decomposing the eosin B, whereas, in energy consumption scale, $UV + H_2O_2$ was found to be the most efficient.

Keywords: Advanced oxidation process; Sonolysis; Eosin B; Hydroxyl radical

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1. Introduction

Ultrasound has been used in a variety of processes such as lysing cells, cleaning surfaces, filtering particles, floatation, drying, emulsification, dissolution, degradation of powder, biological cell disruption and so on [1]. Of late, a considerable interest has been shown by researchers in the decomposition of organic compounds by the use of ultrasound. These include pesticides, volatile organic compounds, sulphite compounds, organic dyes, explosives, and other organic compounds [2]. The ultrasonic process is known to have the unique advantage of completely destroying or converting these compounds (instead of simply transferring to another medium like most conventional treatments). The chemical effects of ultrasound have been reported to take place due to acoustic cavitation, leading to the formation of bubbles, rapid growth and, finally, implosive collapse. According to hot spot theory [3,4], the collapse of a cavitation bubble is almost adiabatic, and it leads to extreme temperatures and pressures inside the bubble. Theoretical calculation yields the temperature as high as 5,000 K and the pressure as high as 1,000 bar inside the bubble. The sonolysis of aqueous solution leads to the formation of three different regions. First is the interior of bubbles where extreme temperatures and pressures exist transiently. In this region, volatile

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solute undergoes decomposition due to pyrolysis in the gas phase and water decomposed to produce H·atoms and OH radicals. The second is the interfacial region between the gas and liquid phases. Although the temperature in this region is relatively lower (compared with the temperature inside the cavity), yet it is high enough to cause thermal decomposition. The third region is the bulk solution where the reaction with hydroxyl radical occurs.

The reaction of pollutants takes place depending on their physical and chemical properties [5]. Hydrophobic and volatile compounds are decomposed mainly by pyrolysis inside the cavitation bubble, whereas hydrophilic compounds are decomposed due to reactions with free radicals in the bulk solution or in the interfacial region depending on the hydrophobicity of the compound.

The organic dyes epitomize a universal class of organic pollutants present in the wastewater in the chemical industry. In fact, the dyes create unyielding environmental problems not only due to their color, but also because of the possible toxic species release during their degradation. In addition, many organic dyes constitute more complex entities, and they are stubborn toward decomposition. Above all, unfortunately, traditional water treatment methods do not remove the dye contaminants and other organics effectively. The combinations of different advanced oxidation process (AOP's) have been found to be effective in decomposing the dyes and other chemicals in the water [6–9].

The AOP's such as photolysis of organic compounds has also emerged as an effective water treatment method over the last decade. The photolytic action dissociates the water molecules resulting in the production of hydroxyl radicals. These radicals cause the decomposition of organic compounds present in the water [10]. Another common method is ozonation. Contrerasa et al. [11] and Azbar et al. [12] documented substantial COD reduction of textile wastewaters after O_3/UV treatment.

We have chosen eosin B, a xanthene dye as the model compound to study the comparative effect of enhancement in sonochemical decomposition using UV, UV/H_2O_2, and ozone.

2. Experimental

Eosin B was obtained from Sigma chemical company. The molecular structure is shown in Fig. 1. H_2O_2 were bought from Merck, Germany and were used as received. The de-ionized water was used to prepare the solution all through this study. Purified oxygen and argon were received from Soxal, Singapore.

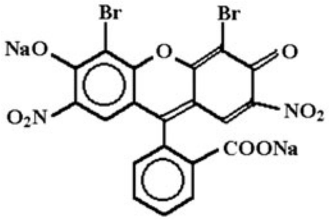

Fig. 1. Molecular structure of eosin B.

Sonication was done using an ultrasonic source (VC-750, sonics and materials). The probe tip was 19 mm in diameter, and the ultrasonic source was employed at 50% amplitude. A water jacketed glass vessel with Teflon cover was used as reaction vessel. The volume of the solution was 200 ml, and the head space was almost zero. The temperature was monitored with the help of a thermocouple immersed in the reacting medium. The frequency of the sound wave was 20 kHz.

The ultraviolet light was supplied by low-pressure ultraviolet lamp located at the top of reactor. The lamp had an output of 8 W at 254 nm. The ozone employed was produced by an ozone generator, which was capable of generating stable levels of O_3 over the required concentration range. The model of the ozone generator used in this study was COM-AD-08, ANSEROS, Germany. By adjusting the generator level or the flow rate of oxygen feed, different concentrations of ozone can be obtained. In our study, we used oxygen as the feed to the ozone generator. All experimental runs were performed at 20°C unless otherwise stated.

The quantitative analysis was done using Shimadzu UV-1601 spectrophotometer. All samples were filtered before analyzing. Shimadzu TOC-5000A analyzer with an ASI-5000 auto sampler was used to analyze the total organic carbon in the samples.

3. Results and discussion

The eosin B disappearance was observed to follow first-order kinetic behavior, while there was no apparent destruction pattern observed for the TOC abatement rates.

3.1. Kinetic comparison

Table 1 summarizes the rate constants for different systems. It can be observed from the table that the combination of different AOP's is very effective in

Table 1
First-order rate constants (in min^{-1}) for eosin B degradation employing different techniques. (T = 20°C)

	Rate constant (min^{-1})
US	0.0083
UV	0.0165
US + H_2O_2	0.0171
US + UV	0.0306
O_3	0.14
UV + H_2O_2	0.235
US + UV + H_2O_2	0.232
US + O_3	0.8

oxidizing eosin B. In this work, it was observed that US/O_3 has the highest rate constant. The rate constant for US/O_3 was 0.8 min^{-1}, which is about 100 times more than the decomposition in ultrasound alone and about 60 times more in case of individual photolytic dissociation. The reaction rate constants from the results of eosin B degradation under combination of different AOP's are in the order: US + O_3 > US + UV + H_2O_2 > UV + H_2O_2 > US + UV > O_3 > US + H_2O_2 > UV > US (Table 1). Being nonvolatile, the sonochemical degradation of eosin B is expected to take place due to hydroxyl radicals in the bulk phase. Joseph et al. [13] also suggested that degradation of azo dyes take place by radical reaction. They attributed it to the absence of products generated in the pyrolytic cleavage of the azo bond. The loss of the chromophoric characteristic in the products and intermediates produced suggests that addition of hydroxyl radicals to the azo double bond is one of the first steps in the degradation process. The much higher enhancement in the combined effect of US and ozone confirmed that the synergy exist between the two processes. Similar findings were reported by other researchers [14–16].

The use of ozone is an established practice in drinking water industry, because not only of its extremely high-oxidizing power, but also its self-decomposition in aqueous solution, resulting in the production of highly reactive OH^- radicals. The synergy, however, could arise from enhanced ozone dissolution, resulting in additional decomposition of ozone (in aqueous and gas phase) causing enhancement in the rates of radical and peroxide production. Besides, the enhancement in rates may also be due to enhanced mass transfer between the bubble and liquid in the presence of ultrasound as reported by Kang et al. [17]. The photolysis, on the other hand, increases the degradation rate by converting the hydrogen peroxide back to OH^- and H^+ radicals. In the ultrasound, the recombination reaction of H^+ and OH^- radicals might have been the cause behind the loss of these radicals for oxidation of the organic compounds.

Of the two; US/O_3 and US/UV-H_2O_2, the former has shown higher degradation rates for eosin B. The degradation was achieved in 5 min for US/O_3, whereas it took 20 min in case of US/UV-H_2O_2. Ozone has the advantage that it acts by dual mechanism; molecular ozone and indirect radical chain type reaction resulting in hydroxyl radicals production. Although the dominant reaction is by hydroxyl radicals, the interaction of molecular ozone with eosin B must have enhanced the reaction rate [18]. Alaton et al. [19] also reported that the quickest color removal for reactive dye bath effluent was achieved in case of ozone compared with UV-H_2O_2.

3.2. Effect of H_2O_2 addition

Hydrogen peroxide decomposition in water leads to the generation of hydroxyl radicals. The effect of hydrogen peroxide was studied to illustrate the implications of hydroxyl radicals on decomposition rate. Fig. 2 shows the degradation curve for eosin B at different H_2O_2 concentration. Significant enhancement was observed in degradation rate for US/UV system.

Under the influences of AOP's, H_2O_2 decomposes as per the reaction [20]:

$$H_2O_2 + \xrightarrow{)))/h\nu} 2HO^{\cdot}$$

$$HO^{\cdot} + H_2O_2 \Rightarrow HO_2^{\cdot} + H_2O$$

$$2HO_2^{\cdot} \Leftrightarrow H_2O_2 + O_2$$

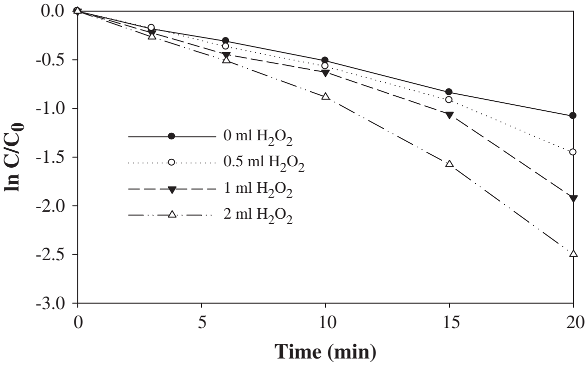

Fig. 2. Effect of hydrogen peroxide on degradation of eosin B.

where))) refers to application of ultrasound and *hv* refers to photolysis.

This complex decomposition formation of H_2O_2 makes the concentration of H_2O_2 almost constant in the system. H_2O_2 was also produced by the reactions of hydroxyl radicals and water.

$$H_2O + OH^{\cdot} \rightarrow H_2O_2 + H^{\cdot}$$

The authors found that the concentration of H_2O_2 remained primarily constant with the time. This way H_2O_2 acts as pseudocatalyst enhancing the rate of reaction. They observed increase in rate constant with the increase in H_2O_2 concentration. However, in their study, on the ultrasonic decomposition of humic substances, Chemat et al. [21] found that the H_2O_2 must be kept at optimum levels. They reported inhibition of rate degradation at higher concentration of H_2O_2. This probably could be due to scavenging of OH radicals by H_2O_2.

It is also observed that during the initial period, eosin B degradation was almost similar at all H_2O_2 concentration (including no H_2O_2). Water thermolysis naturally yields OH radicals, and this coupled with the presence of H_2O_2 may lead to same OH radicals concentration during the initial period of reaction. As the reaction proceeds due to addition of H_2O_2, OH radicals concentration would increase leading to increased reaction rate.

3.3. Effect of dissolved gas

The cavitational effect of ultrasound causes the degassing of liquids. Therefore, many researchers deliberately bubble the gas through a sonochemical reaction to facilitate uniform cavitation [22]. We studied the effect of argon, nitrogen, and oxygen on the decomposition rate. The degradation curves are presented in Fig. 3. The rate enhancement under Ar is considerably higher than that of the other two gases. The nature of the dissolved gas is an important factor, since the amount of OH radicals produced depends on the type of gas dissolved [23]. They reported that the hydroxyl radical production is higher in Ar-saturated solution at 20 kHz frequency. The reaction rate constants for hydroxyl radical production was 0.103 μM min^{-1} for Ar-saturated solution as compared to 0.0699 μM min^{-1} for O_2-saturated solution. Similar observations were also made by Joseph et al. [13], who reported 10% enhancements under Ar as compared to air and O_2 for all the organic dyes tested. These results confirmed that the OH radicals are the dominant factor in the decomposition of eosin B.

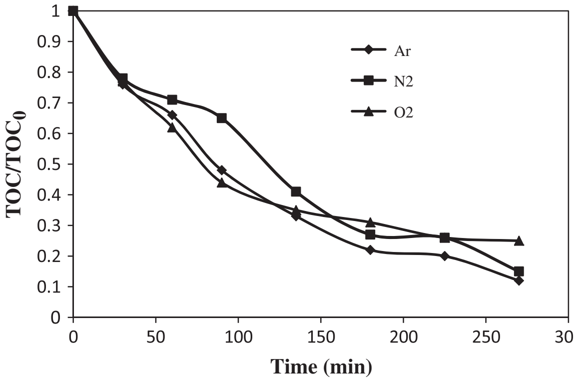

Fig. 3. Mineralization of eosin B under different saturated gas.

3.4. Effect of temperature

The effect of temperature was studied by varying the water bath temperature. The temperature inside the reactor is normally 10–12˚C greater than that of bath. Because of the low vapor pressure, eosin B will behave differently under the influence of temperature. We observed that the rate showed a constant decreasing trend with the increase in temperature. It was also found that as the k decreased from $k = 0.0176\,\text{min}^{-1}$ at 10˚C to $k = 0.0038\,\text{min}^{-1}$ at 40˚C for 30 μM initial concentration. Equivalent results were found for 15 μM. The degradation curves (for 15 μM) are given in Fig. 4. In this work, we have used eosin B whose solubility is quite high (39%). Therefore, we assume that the amount of diffusion of eosin molecule would be very less, even at high vapor pressure causing less decomposition at high temperature.

Contradictory results have been reported in the literature regarding the effect of temperature on sonochemical degradation. Ku et al. [24] observed a similar trend of decrease in reaction rate of 2-chlorophenol with the increase in temperature. Similar results were observed by Emery et al. [25]. The degradation of triphenylphosphine oxide in water, a toxic compound typically found in effluents from the pharmaceutical industry, decreases as temperatures rises through 5, 20, 35, 50, and 70˚C. Kim et al. [26], however, observed that the rate constant of dibenzothiophene was increasing with increasing temperature in the range of 15–50˚C. They attributed it to diffusion-controlled reaction mechanism.

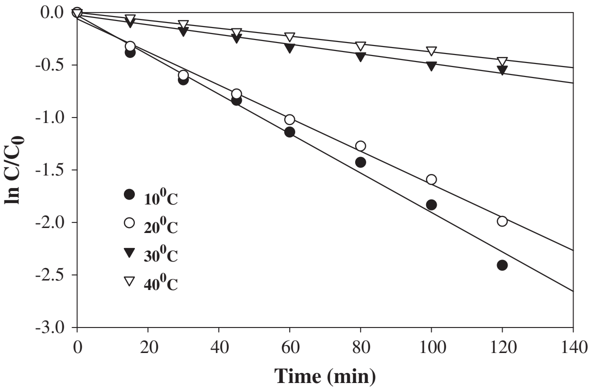

Fig. 4. Effect of temperature on degradation of eosin B.

3.5. Effect of pH

In wastewater treatment, the pH value is a very crucial parameter that need always be taken into consideration. In this case, since both ozonation and sonication depend on the pH of the aqueous stream to be treated; experiments were conducted in the pH range 3–11, for both US/O_3 and ozonation. It was noted that degradation of eosin B is quite fast irrespective of the solution pH for US/O_3. However, the O_3 alone has shown higher degradation under acidic conditions. It is believed that additional $OH^{\cdot}$ scavenging by HCO_3^-/CO_3^{2-} might occur at alkaline pH values. Duque et al. [8] noted that crystal violet dye (CV) degradation evolution under the three pH conditions was similar. In all of the cases, a sonochemical CV conversion of 50 and 90% was reached after 30 and 180 min, respectively. Hamdaoui and Naffrechoux [27] observed that the sonolytic degradation was quite effective at low pH. When an aqueous 4-CP solution at pH 5.5 was subjected to sonication, the degradation occurred with a lifetime of 70 min. Under alkaline conditions (pH 12.7), 4-CP the degradation took 160 min. Similarly, Chen and Huang [28] noted the increased sonochemical degradation of nitrotoluenes under acidic conditions. On the other hand, diclofenac reduction was found to be higher in alkaline conditions [29]. No significant difference in rate constants was observed within the acidic-neutral range (Fig. 5).

3.6. Mineralization

The extent of mineralization of eosin B was studied to ensure the complete conversion of eosin B to harmless CO_2 and other products. The rate of mineralization was found to be very slow for all the experiments. For example, 60% TOC reduction was achieved for US/O_3 in 4 h, whereas complete degradation was achieved in only 5 min. Our results suggest that the presence of H_2O_2 was a significant factor in TOC removal. Fig. 6 summarizes the results obtained with combined action of US/UV at different H_2O_2 concentration. The TOC value reduces with the increase in concentration of H_2O_2. As mentioned above, amount of hydroxyl radicals produced is higher in Ar saturated solution. The large amount of hydroxyl radicals will certainly make it easier for intermediates to decompose to CO_2.

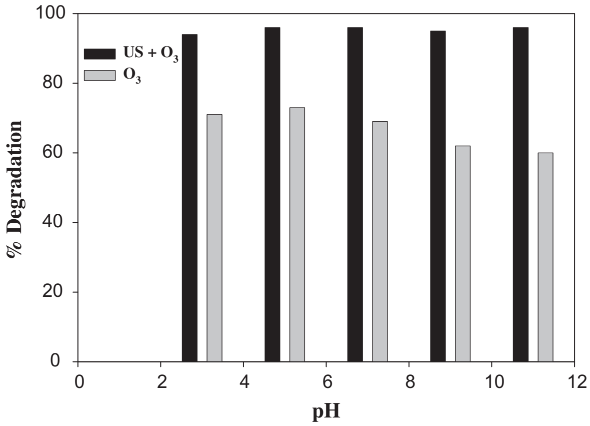

Fig. 5. pH effect on degradation of eosin B under ozonation and combined US/O_3.

It was also observed that individual sonolysis or photolysis hardly mineralizes the eosin B. Thus, the combination of US with other process was very effective for mineralization of organic dye.

3.7. Energy consumption

Any water treatment process will not be beneficial unless, it is cost-effective. The aspect of energy

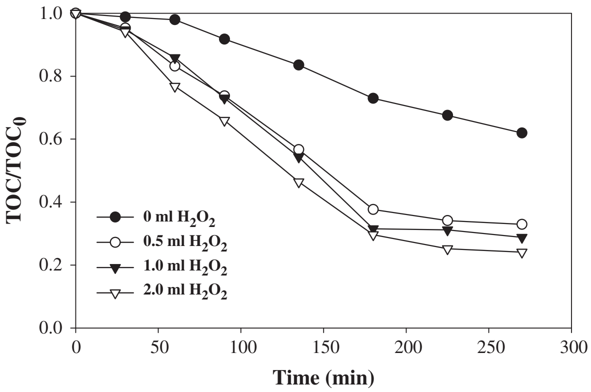

Fig. 6. Mineralization of eosin B under combined action of US/UV at different H_2O_2 concentration.

Table 2
EE/O values for various AOP’s ($C_0 = 15\,\mu M$; $T = 20^\circ C$)

System	Parameters	EE/O (KWh/m^3/order)
US	$P = 375\,W$; $f = 20\,kHz$	7,100
UV	$P = 8\,W$	310
US + H_2O_2	$P = 375\,W$; $f = 20\,kHz$; Molar ratio (H_2O_2/eosin B) = 160–644	4,200–6,250
US + UV	$P_{US} = 375\,W$; $P_{UV} = 8\,W$	2,480
US + UV + H_2O_2	$P_{US} = 375\,W$; $P_{UV} = 8\,W$; Molar ratio (H_2O_2/eosin B) = 160–644	600–2,000
O_3	$P_{ozonator} = 400\,W$	350
US + O_3	$P_{US} = 375\,W$ $P_{ozonator} = 400\,W$	215
UV + H_2O_2	$P_{UV} = 8\,W$; Molar ratio (H_2O_2/eosin B) = 644	35

consumption is hardly discussed in the literature. A normalized coefficient electrical energy per order (EE/O) was used to see the efficacy of various systems [30]. The equation for EE/O is as follows:

$$\text{EE/O(in KWh/m}^3\text{/order)} = \frac{P \times 1,000 \times t_t}{V \times 60 \times \log(c_i/c_f)}$$

where P is the rated power (kW), V is the volume (L) of water treated in the time t_t (in min), c_i, c_f are the initial and final concentrations (mol L^{-1}) of contaminant in the water. Higher EE/O values would correspond to lower destruction efficiencies.

The results for various systems are summarized in Table 2. Based on the table, we can conclude the following energy consumption scale: US > US + UV > US + UV + H_2O_2 > US + O_3 > UV + H_2O_2. The high EE/O value indicates less energy efficient system. Though it does not include the capital cost and other costs related to operation, EE/O value does indicate the power consumption for the treatment process.

One of the primary limitations of ultrasonic system is its poor energy efficiency. Although the process has the advantage of decomposing the compounds in the cavitation bubble in addition to hydroxylation, the high-energy requirement remains a stumbling block. The suitable mechanism of using ultrasound with low-energy input will be very beneficial in the scale up of sono-chemical system.

4. Conclusion

Based on the experiments conducted, it can be concluded:

(1) The enhancement in sonochemical decomposition was achieved by employing the combinations of various AOP’s. The kinetic analysis indicate that the US + O_3 was faster in decomposing the eosin B than UV + H_2O_2. But, in energy consumption scale, UV + H_2O_2 was found to be more efficient.
(2) The addition of H_2O_2 significantly enhanced the reaction rate for US/UV system.
(3) The rate enhancement under Ar is considerably higher than that of N_2 and O_2. This result shows that the decomposition mechanism may be by reaction with hydroxyl radicals.
(4) The rate constant was found to be temperature-dependent in the range 10–40°C. It decreases with the increase in temperature.
(5) pH variation showed minimal effects on the rate of dye degradation.

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