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### Ultrasonic degradation of Rodamin 6G in the presence of hydrogen peroxide and Zinc Oxide

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#### KEYWORDS

Ultrasonic degradation, Rodamin, Zinc Oxide

#### A B S T R A C T

Dyestuffs are often present in industrial wastewaters and can consist of hazardous substances have a serious impact on the environment and personal health. Sonochemical degradation which combines destruction of the target compounds by free radical reaction and thermal cleavage is one of the recent advanced oxidation processes (AOP) and proven to be effective for removing low concentration organic pollutants from aqueous streams. The aim of this study is to investigate the effect of operational parameters such as solution pH value, addition amount of ZnO catalyst, addition amount of H<sub>2</sub>O<sub>2</sub> and power ultrasound on the ultrasonic degradation of Rhodamine 6G(R6G) in aqueous solution. The results showed that decolorization of R6G follows pseudo-first-order reaction kinetics. The optimal conditions for high degradation ratios of R6G are considered to be the solution acidities of pH 9.0, the addition amounts of 2.0 g/L ZnO catalyst and the addition amounts of H<sub>2</sub>O<sub>2</sub> 0.02 mol/L, respectively, for the initial concentration of R6G 2.087×10<sup>-5</sup> mol/L. In addition, the rate of degradation was increased by increasing power ultrasound.

#### Introduction

The excess use of various dyes in the textile industry has led to the severe surface water and groundwater contamination by releasing the toxic and colored effluents, which are important for the sake of increasing amount, its variety and resistance to biological destruction (1). Various chemical and physical processes such as precipitation, adsorption, air stripping,

flocculation, reverse osmosis and ultrafiltration can be used for color removal from textile effluents (2-5). However these techniques are non-destructive, since they only transfer the non-biodegradable matter into sludge, giving rise to new type of pollution, which needs further treatment(6-8).

Recently, ultrasonics was found to be a very suitable method for the degradation of organic compounds (9, 10). The ultrasonic irradiation of liquids generates cavitation bubbles, which grow during the compression/rarefaction cycles until they reach a critical species. Inside cavitation bubbles, the temperature and pressure rise to the order of 5000 K and 100MPa, respectively (11). Under such extreme conditions during bubble collapse, organic compounds are degraded by direct pyrolysis and hydroxyl free radical oxidation ( $\cdot\text{OH}$ ) reactions (12). With direct pyrolysis an organic compound absorbed in a cavitation bubble is converted to by-products due to the extremely high temperature and pressure inside the bubble. Under these extreme conditions, free radicals are also formed when water molecules are split (13):



These radicals can react with contaminants to form byproducts. The main degradation pathway is direct pyrolysis, but in the presence of oxidants such as  $\text{O}_3$  and  $\text{H}_2\text{O}_2$ , radicals produced in implosive bubbles can also be an important reaction pathway (14).

The aim of this study is to investigate the effect of operational parameters such as solution pH value, addition amount of ZnO catalyst, addition amount of  $\text{H}_2\text{O}_2$  and power ultrasound on the ultrasonic degradation of Rhodamine 6G, which is an important dye used in textile industry, in aqueous solution.

## Experimental

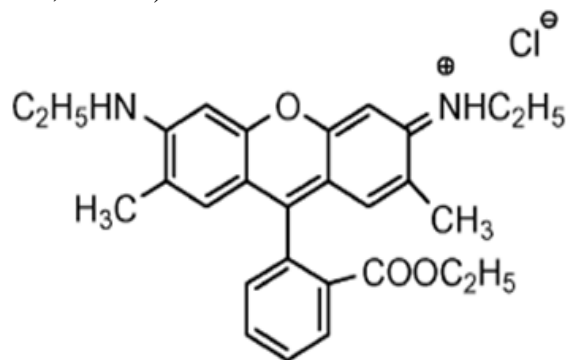
### Materials

Rhodamine 6G (Fig.1), Sodium di hydrogen phosphate salt, hydrogen peroxide were further supplied by Merck, Zinc oxide was further supplied by Floka. All materials were used without purification. Distilled

water was used for preparation of solutions. pH of the solutions was adjusted with 1M HCl and 1M NaOH.

### Apparatus and procedure

Stock solution of R6G ( $2.087 \times 10^{-5}$  mol/L) was prepared gravimetrically by an analytical balance (Sartorius CP224 S) with a precision of  $\pm 1 \times 10^{-4}$  g. Others R6G solutions were prepared from the stock solution. For ultrasonic degradation 10 mL of R6G solution were sonicated by an ultrasonic generator (Dr. Hielscher UP400 S ultrasonic processor) with an H3 sonotrode with diameter 3 mm. The frequency of the ultrasound was 24 kHz. Periodically, samples were removed and their UV-Vis absorption was monitored with T80 UV/Vis spectrophotometer (PG Instruments Ltd). The temperature of solutions was kept constant by a temperature controller (RW-525G, Korea.)



Rhodamine 6G

**Fig.1** Chemical structure of Rhodamine 6G

## Result and discussion

### The effect of pH

#### Effect of pH on the ultrasonic degradation of R6G in the presence of hydrogen peroxide

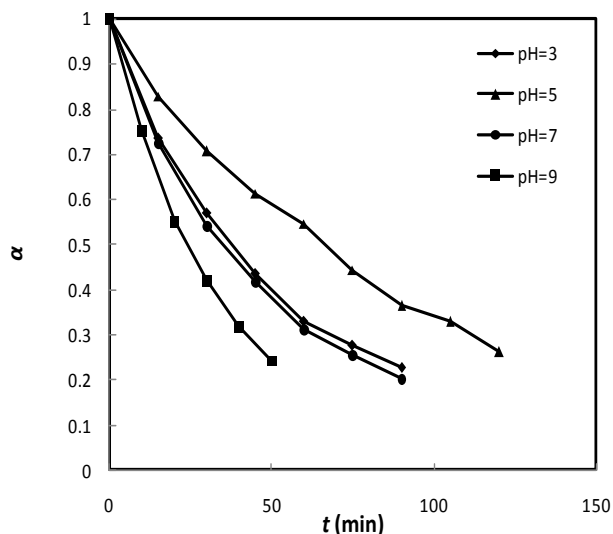
The solution pH value is an important factor that can influence the ultrasonic degradation

of various organic pollutants. To study the effect of pH on the rate of degradation, experiments were carried out at various pH 3,5,7,9 values, for constant dye concentration ( $2.087 \times 10^{-5}$  mol/L) in the presence of hydrogen peroxide with concentration 0.02 mol/L and ultrasound power 400 W at a temperature of 25 °C. In all the experiments, the pH values were adjusted by adding appropriate amount of 1 mol/L HCl and 1 mol/L NaOH aqueous solutions. The concentration of R6G was calculated from the absorption in  $\lambda_{\max} = 526$  nm by using a calibration curve and Beer's Law. Then unreacted fractions of R6G,  $\alpha$ , were evaluated. The relationship between  $\alpha$  and degradation time is shown in Fig. 2. The relationship between  $\ln(\alpha)$  and degradation time shows a linear relationship which suggests that the degradation of R6G is a pseudo-first-order reaction. Thus the rate equation for degradation of R6G can be written as:

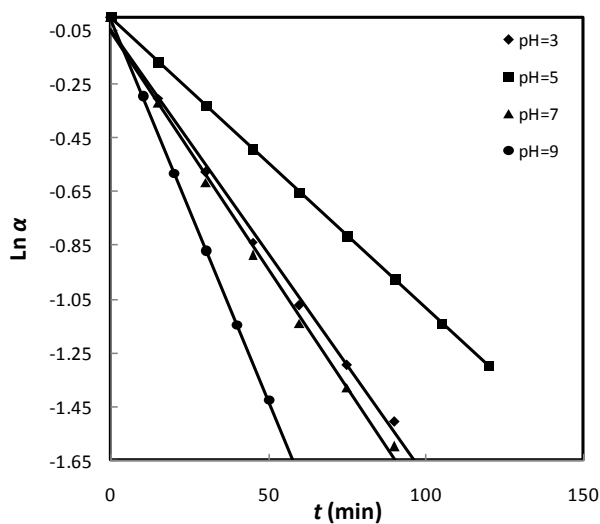
$$\ln \frac{[R6G]}{[R6G]_0} = \ln(\alpha) = -k' t$$

where  $k'$  is the apparent rate constant. The apparent rate constants were obtained from the slope of  $\ln(\alpha)$  versus time. The relationship between  $\ln(\alpha)$  and degradation time is shown in Fig. 3. The apparent rate constant for degradation of R6G at 25 °C at various pH 3,5,7,9 values were obtained as  $1.66 \pm 0.02 \times 10^{-2}$ ,  $1.08 \pm 0.02 \times 10^{-2}$ ,  $1.77 \pm 0.02 \times 10^{-2}$ ,  $2.8 \pm 0.02 \times 10^{-2} \text{ min}^{-1}$ , respectively. Our results indicate that rate of degradation decreases with increasing of solution pH value from 3 to 5, but the rate of degradation after pH 5 increases with increasing pH values. It would appear that the possible protonation of nitrogen in the secondary amine group of the xanthenes ring must occur at low pH values, but at high pH values are free electron pair on the amine nitrogen therefore transfers charge from

amine nitrogen to aromatic rings and aromatic rings have more activity and contributes in degradation reaction(15).



**Fig.2** Relationship between unreacted fraction of R6G and degradation time with  $(R6G)_0 = 2.087 \times 10^{-5} \text{ mol L}^{-1}$ ,  $(H_2O_2)_0 = 0.02 \text{ mol L}^{-1}$  and US 400W at 25 °C.



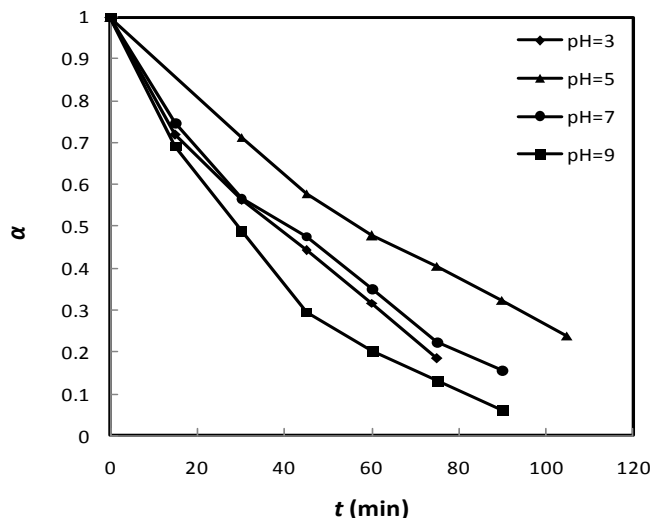
**Fig.3** Relationship between  $\ln(\alpha)$  and degradation time with  $(R6G)_0 = 2.087 \times 10^{-5} \text{ mol L}^{-1}$ ,  $(H_2O_2)_0 = 0.02 \text{ mol L}^{-1}$  and US 400W at 25 °C.

### Effect of pH on the ultrasonic degradation of R6G in the presence of hydrogen peroxide and Zinc oxide

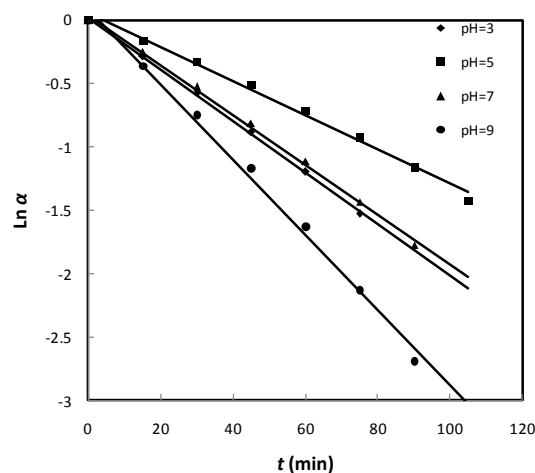
To study the effect of pH on the rate of degradation, experiments were carried out at various pH 3,5,7,9 values, for constant dye concentration ( $2.087 \times 10^{-5}$  mol/L) in the presence of hydrogen peroxide with concentration 0.02 mol/L and amount of catalyst (1gr/L) and ultrasound power 400 W at a temperature of 25 °C. In all the experiments, the pH values were adjusted by adding appropriate amount of 1 mol/L HCl and 1 mol/L NaOH aqueous solutions.

The unreacted fractions of R6G were calculated from the absorption spectra by using a calibration curve and Beer's Law. The relationship between  $\alpha$  and degradation time is shown in Fig. 4. The relationship between  $\ln(\alpha)$  and degradation time shows a linear relationship which suggest that the degradation of R6G is a pseudo-first-order reaction.

The apparent rate constants were obtained from the slope of  $\ln(\alpha)$  versus time. The relationship between  $\ln(\alpha)$  and degradation time is shown in Fig. 5. The apparent rate constant for degradation of R6G at 25 °C at various pH 3,5,7,9 values were obtained as  $2.04 \pm 0.02 \times 10^{-2}$ ,  $1.35 \pm 0.02 \times 10^{-2}$ ,  $1.96 \pm 0.02 \times 10^{-2}$ ,  $2.97 \pm 0.02 \times 10^{-2} \text{ min}^{-1}$ , respectively. It is obvious that the rate of degradation of R6G in the presence of ZnO particles is higher than the absence of ZnO particles. Increasing of rate of degradation in the presence of ZnO particles is due to adsorption of R6G on the surfaces of ZnO particles.



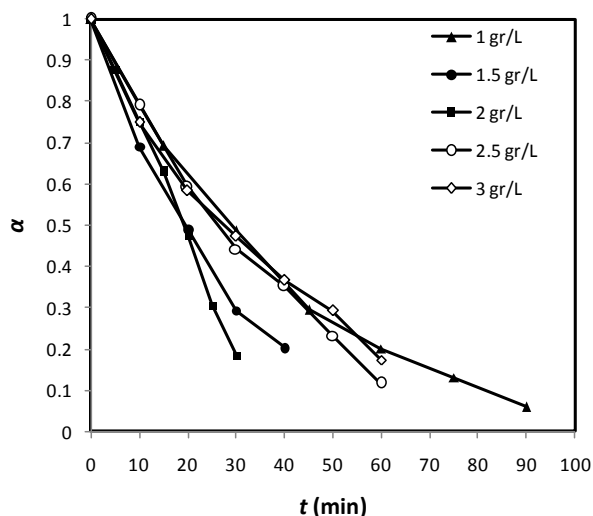
**Fig.4** Relationship between unreacted fraction of R6G and degradation time with  $(R6G)_0 = 2.087 \times 10^{-5} \text{ mol L}^{-1}$ ,  $(H_2O_2)_0 = 0.02 \text{ mol L}^{-1}$ ,  $(ZnO)_0 = 1 \text{ gL}^{-1}$  and US 400W at 25 °C.



**Fig.5** Relationship between  $\ln(\alpha)$  and degradation time with  $(R6G)_0 = 2.087 \times 10^{-5} \text{ mol L}^{-1}$ ,  $(H_2O_2)_0 = 0.02 \text{ mol L}^{-1}$ ,  $(ZnO)_0 = 1 \text{ gL}^{-1}$  and US 400W at 25 °C.

**The effect of ZnO addition amount on the sonocatalytic degradation of R6G in the presence of hydrogen peroxide**

In order to determine the effect of the addition amount of ZnO particales, experiments were performed with different amounts from 1 to 3 g/L for constant dye concentration( $2.087 \times 10^{-5}$  mol/L) at pH 9. The unreacted fractions of R6G were calculated from the absorption spectra by using a calibration curve and Beer's Law. The relationship between  $\alpha$  and degradation time is shown in Fig. 6. The relationship between  $\ln(\alpha)$  and degradation time shows a linear relationship which suggest that the degradation of R6G is a pseudo-first-order reaction.

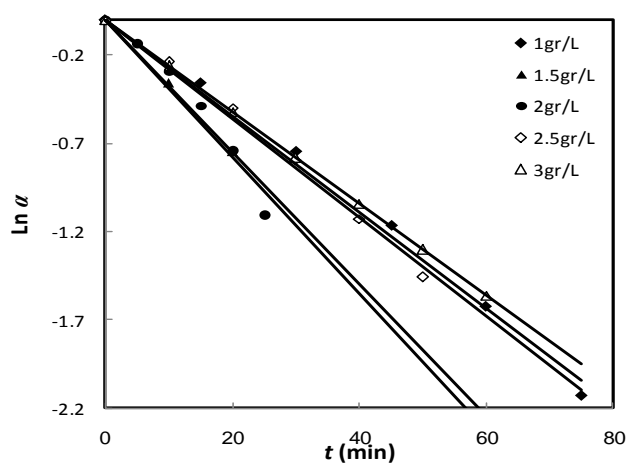


**Fig.6** Relationship between unreacted fraction of R6G and degradation time with  $(R6G)_0 = 2.087 \times 10^{-5}$  mol L<sup>-1</sup>,  $(H_2O_2)_0 = 0.02$  mol L<sup>-1</sup>,  $(ZnO)_0 = 1, 1.5, 2, 2.5, 3$  gL<sup>-1</sup> and US 400W at 25 °C.

The apparent rate constants were obtained from the slope of  $\ln(\alpha)$  versus time. The relationship between  $\ln(\alpha)$  and degradation time is shown in Fig. 7. The apparent rate constant for degradation of R6G at 25 °C at different amounts of ZnO particales from 1 to 3 g/L were obtained as  $2.73 \pm 0.02 \times 10^{-2}$ ,

$3.74 \pm 0.02 \times 10^{-2}$ ,  $3.87 \pm 0.02 \times 10^{-2}$ ,  $2.8 \pm 0.02 \times 10^{-2}$ ,  $2.6 \pm 0.02 \times 10^{-2}$  min<sup>-1</sup>, respectively. Our results showe that the sonocatalytic degradation ratios of R6G increases with the increase of ZnO particles up to 2.0 g/L.

And then the degradation ratio of R6G decreases to some extent after the addition amount of 2.5 g/L. This phenomenon may be due to the nearness and aggregation of superfluous ZnO particles one another at high addition amount, which causes disturb the transmission of ultrasound in water medium(1).



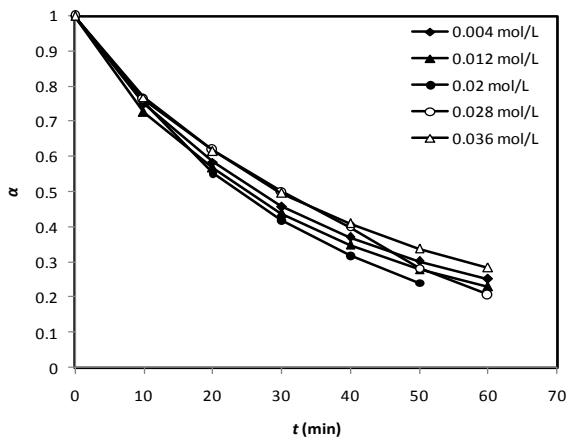
**Fig.7** Relationship between  $\ln(\alpha)$  and degradation time with  $(R6G)_0 = 2.087 \times 10^{-5}$  mol L<sup>-1</sup>,  $(H_2O_2)_0 = 0.02$  mol L<sup>-1</sup>,  $(ZnO)_0 = 1, 1.5, 2, 2.5, 3$  gL<sup>-1</sup> and US 400W at 25 °C.

**The effect of H<sub>2</sub>O<sub>2</sub> addition**

In order to determine the effect of H<sub>2</sub>O<sub>2</sub> addition, experiments were performed with different amounts from 0.004 to 0.036 mol/L for constant dye concentration( $2.087 \times 10^{-5}$  mol/L) at pH 9.0. The unreacted fractions of

R6G were calculated from the absorption spectra by using a calibration curve and Beer's Law. The relationship between  $\alpha$  and degradation time is shown in Fig. 8. The relationship between  $\ln(\alpha)$  and degradation time shows a linear relationship which suggest that the degradation of R6G is a pseudo-first-order reaction.

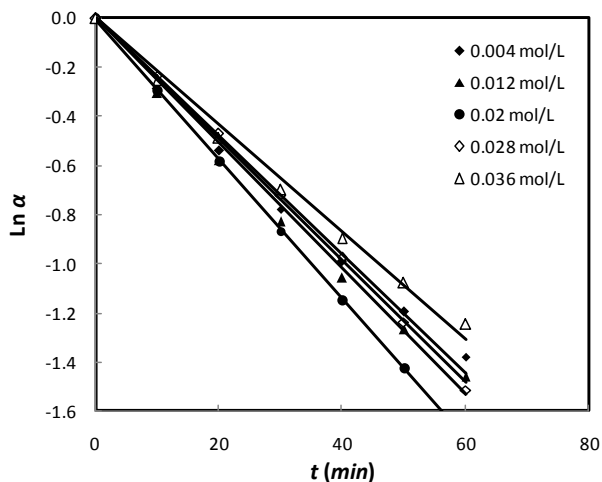
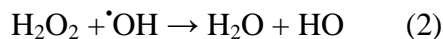
The apparent rate constants were obtained from the slope of  $\ln(\alpha)$  versus time. The relationship between  $\ln(\alpha)$  and degradation time is shown in Fig. 9. The apparent rate constant for degradation of R6G at 25 °C at different amounts of  $\text{H}_2\text{O}_2$  addition from 0.004 to 0.036 mol/L were obtained as  $2.29 \pm 0.02 \times 10^{-2}$ ,  $2.42 \pm 0.02 \times 10^{-2}$ ,  $2.85 \pm 0.02 \times 10^{-2}$ ,  $2.47 \pm 0.02 \times 10^{-2}$ ,  $2.07 \pm 0.02 \times 10^{-2} \text{ min}^{-1}$ , respectively. The results show that the removal rate increases with increasing  $\text{H}_2\text{O}_2$  concentration up to 0.02 molL<sup>-1</sup>.



**Fig.8** Relationship between unreacted fraction of R6G and degradation time with  $(\text{R6G})_0 = 2.087 \times 10^{-5} \text{ mol L}^{-1}$ ,  $(\text{H}_2\text{O}_2)_0 = 0.004, 0.012, 0.02, 0.028, 0.036 \text{ mol L}^{-1}$  and US 400W at 25 °C.

This is as a result of formation of more hydroxyl radicals from hydrogen peroxide decomposition. Above 0.02 molL<sup>-1</sup> the reaction rate decreases with increasing hydrogen peroxide concentration. This is reasonable, since when  $\text{H}_2\text{O}_2$  concentration

reaches above a critical value,  $\cdot\text{OH}$  and  $\cdot\text{H}$  generated by the thermolysis of water in the solution medium efficiently reacts with  $\text{H}_2\text{O}_2$ , which is a  $\cdot\text{OH}$  scavenger as follows (16):

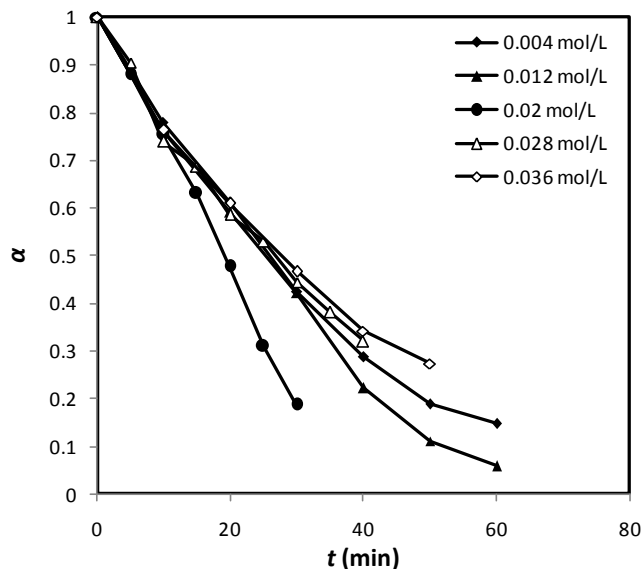


**Fig.9** Relationship between  $\ln(\alpha)$  and degradation time with  $(\text{R6G})_0 = 2.087 \times 10^{-5} \text{ mol L}^{-1}$ ,  $(\text{H}_2\text{O}_2)_0 = 0.004, 0.012, 0.02, 0.028, 0.036 \text{ mol L}^{-1}$  and US 400W at 25 °C.

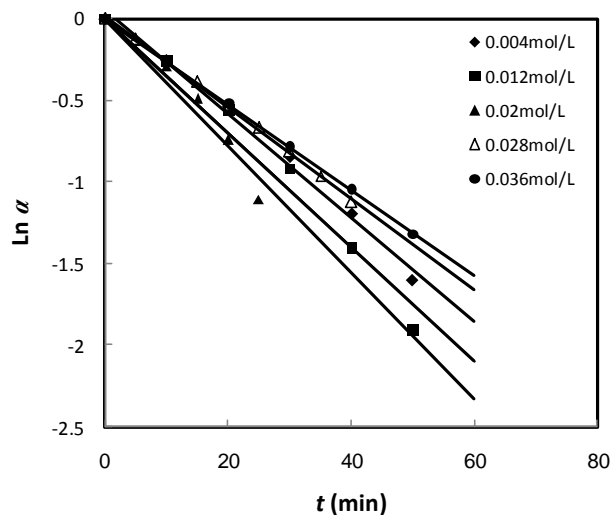
### The effect of $\text{H}_2\text{O}_2$ addition in the presence of ZnO particals

In order to determine the effect of  $\text{H}_2\text{O}_2$  addition in the presence of ZnO particals, experiments were performed with different amounts  $\text{H}_2\text{O}_2$  from 0.004 to 0.036 mol/L for constant dye concentration ( $2.087 \times 10^{-5} \text{ mol/L}$ ) and ZnO with concentration 2.0 g/L at pH 9.0. The unreacted fractions of R6G were calculated from the absorption spectra by using a calibration curve and Beer's Law. The relationship between  $\alpha$  and degradation time is shown in Fig. 10. The relationship between  $\ln(\alpha)$  and degradation time shows a linear relationship which suggest that the degradation of R6G is a pseudo-first-order reaction.

The apparent rate constants were obtained from the slope of  $\ln(\alpha)$  versus time. The relationship between  $\ln(\alpha)$  and degradation time is shown in Fig. 11.



**Fig.10** Relationship between unreacted fraction of R6G and degradation time with  $(R6G)_0 = 2.087 \times 10^{-5} \text{ mol L}^{-1}$ ,  $(H_2O_2)_0 = 0.004, 0.012, 0.02, 0.028, 0.036 \text{ mol L}^{-1}$ ,  $(ZnO)_0 = 2.0 \text{ g/L}$  and US 400W at  $25^\circ \text{C}$ .



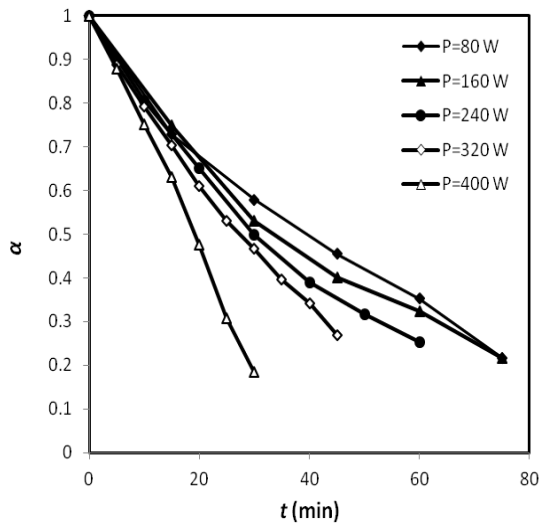
**Fig.11** Relationship between  $\ln(\alpha)$  and degradation time with  $(R6G)_0 = 2.087 \times 10^{-5} \text{ mol L}^{-1}$ ,  $(H_2O_2)_0 = 0.004, 0.012, 0.02, 0.028, 0.036 \text{ mol L}^{-1}$ ,  $(ZnO)_0 = 2.0 \text{ g/L}$  and US 400W at  $25^\circ \text{C}$ .

The apparent rate constant for degradation of R6G at  $25^\circ \text{C}$  at different amounts of  $H_2O_2$  addition from 0.004 to 0.036 mol/L were obtained as  $3.19 \pm 0.02 \times 10^{-2}$ ,  $3.5 \pm 0.02 \times 10^{-2}$ ,  $3.87 \pm 0.02 \times 10^{-2}$ ,  $2.8 \pm 0.02 \times 10^{-2}$ ,  $2.61 \pm 0.02 \times 10^{-2} \text{ min}^{-1}$ , respectively.

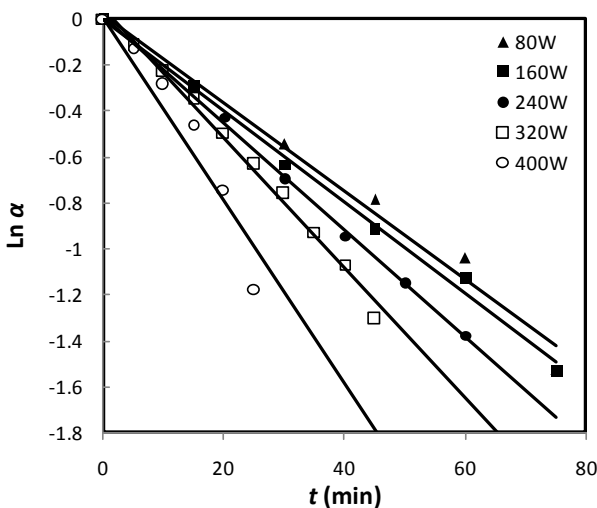
### The effect of ultrasound power

One important factor that influences the performance of the ultrasonic degradation is the ultrasound power. Degradation of R6G was carried out at pH 9.0 in the presence of (hydrogen peroxide+ Zinc oxide) with different ultrasound power. The unreacted fractions of R6G were calculated from the absorption spectra by using a calibration curve and Beer's Law. The relationship between  $\alpha$  and degradation time is shown in Fig. 12. The relationship between  $\ln(\alpha)$  and degradation time shows a linear relationship which suggest that the degradation of R6G is a pseudo-first-order reaction.

The apparent rate constants were obtained from the slope of  $\ln(\alpha)$  versus time. The relationship between  $\ln(\alpha)$  and degradation time is shown in Fig. 13. The apparent rate constant for degradation of R6G at  $25^\circ \text{C}$  at different ultrasound power were obtained as  $1.92 \pm 0.02 \times 10^{-2}$ ,  $1.99 \pm 0.02 \times 10^{-2}$ ,  $2.33 \pm 0.02 \times 10^{-2}$ ,  $2.83 \pm 0.02 \times 10^{-2}$ ,  $3.87 \pm 0.02 \times 10^{-2} \text{ min}^{-1}$ , respectively. The rate constants of degradation of R6G using different output powers (manufacturer's values, not calorimetric) indicate that the rate of degradation of R6G is increased by increasing output powers. This may be due to the enhancement of rate of the formation of hydroxyl radicals by ultrasound.



**Fig.12** Relationship between unreacted fraction of R6G and degradation time with  $(R6G)_0 = 2.087 \times 10^{-5} \text{ mol L}^{-1}$ ,  $(H_2O_2)_0 = 0.02 \text{ mol L}^{-1}$ ,  $(ZnO) = 2.0 \text{ g L}^{-1}$  and US with different power at  $25^\circ \text{C}$ .



**Fig.13** Relationship between  $\text{Ln}(\alpha)$  and degradation time with  $(R6G)_0 = 2.087 \times 10^{-5} \text{ mol L}^{-1}$ ,  $(H_2O_2)_0 = 0.02 \text{ mol L}^{-1}$ ,  $(ZnO) = 2.0 \text{ g L}^{-1}$  and US with different power at  $25^\circ \text{C}$ .

## Conclusion

In this study, ultrasonic degradation of R6G, was studied using sonication. The effect of operational parameters such as pH, ZnO and  $H_2O_2$  concentrations and ultrasound power were investigated on the removal rate of R6G. The removal rate of R6G follows pseudo-first-order kinetic. The optimal conditions for high degradation ratios of R6G are considered to be the solution acidities of pH 9.0, the addition amounts of 2.0 g/L ZnO particals and the addition amounts of  $H_2O_2$  0.02 mol/L, respectively, for the initial concentration of R6G  $2.087 \times 10^{-5} \text{ mol/L}$ . In addition, the rate of degradation was increased by increasing ultrasound power.

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