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Comparison of Sonocatalytic Activities on the Degradation of Rhodamine B in the Presence of TiO₂ Powder and Nanotubes

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Abstract: Titanium dioxide (TiO₂) powder and TiO₂ nanotubes (NTs) were used as the catalysts for sonocatalytic degradation of Rhodamine B in aqueous solution. The effect of parameters such as initial concentration of between 50-150 mg L⁻¹, catalyst loading of between 500-3000 mg L⁻¹, solution temperature of between 20-70°C, hydrogen peroxide (H₂O₂) concentration of between 4-16 mM and the presence of air flow at ultrasonic power of 50 W and 35 kHz had been investigated. Then, the optimum condition for sonocatalytic degradation Rhodamine B had been established. Higher sonocatalytic degradation efficiency of Rhodamine B can be achieved through TiO₂ nanotubes as compared to TiO₂ powder. The experimental results show that the best degradation efficiency of Rhodamine B can be obtained when the experimental conditions occurred at the initial concentration of 50 and 2000 mg L⁻¹ of TiO₂ NTs, 8 mM of H₂O₂, ultrasonic power of 50 W and frequency of 35 kHz with the presence of air flow which give the efficiency of above 85% in 120 min.

Key words: Sonocatalytic, Rhodamine B, titanium dioxide, powder, nanotubes

INTRODUCTION

Presently, there is over 7×10^5 tons annual worldwide production of dyes has been reported in the literature and it is estimated that 10-15% of the dyestuff is lost in the effluent during the dyeing processes (Abdullah and Ling, 2010). Methods such as coagulation, filtration and adsorption by activated carbon are only able to transfer the organic pollutants from one phase to another (Inoue *et al.*, 2006). Besides, the presence of one or several benzene rings in the dye structure can always cause conventional treatment process to be ineffective in degrading and destroying these organic pollutants. Aromatic ring is a highly stable compound which is hardly degraded by using chemical and biological methods (Wang *et al.*, 2007c). Therefore, a lot of studies have been dedicated to treat this wastewater by using advanced oxidation process which involves hydroxyl (\bullet OH) radicals to mineralize the organic compounds (Abbasi and Asl, 2008; Harir *et al.*, 2009; Shimizu *et al.*, 2007; Wang *et al.*, 2007b).

The method of ultrasonic irradiation is usually used to treat some dyestuff wastewaters owing to its advantages such as cleanliness, high efficiency and non-secondary pollution generated (Wang *et al.*, 2007a). Application of ultrasounds in water will cause the chemical effect of acoustic cavitation which represented by the formation, growth and implosive collapse of

cavities. The temperature and pressure could rise up to 5000 K and 100 MPa, respectively inside the cavitation bubbles (Abdullah and Ling, 2010; Merouani *et al.*, 2010). When water is sonicated, some reactive radicals such as \bullet OH, \bullet H and \bullet OOH are produced, the former radical being a strong oxidizing agent which able to react actively with organic compounds.

In the sonocatalytic degradation of organic dye, the TiO₂ was used as sonocatalyst because of its biological and chemical properties such as high catalytic activity, high chemical stability, inexpensive and low toxicity (Deng *et al.*, 2009; Wang *et al.*, 2007a). Many researchers have shown that the presence of TiO₂ could increase the sonocatalytic degradation of organic pollutants (Abdullah and Ling, 2010; Wang *et al.*, 2007a; Tuziuti *et al.*, 2005). Recently, there are a few studies using modification of TiO₂ such as mixing with other elements (rare metals, rare-earth metals) through doping or composite method in order to restrain the recombination of generated holes and electron pairs in addition to reduce the energy band gap of anatase TiO₂ powder (Wang *et al.*, 2008b, 2009, 2010). This could enhance the sonocatalytic degradation efficiency of organic dyes.

The aim of this study is to investigate the effect of sonocatalytic degradation using titanium dioxide nanotubes (TiO₂ Nts) as compared to TiO₂ powder. In this study, the TiO₂ NTs were prepared by the combination of sol-gel process with hydrothermal

treatment before treating the organic dye in aqueous solution under ultrasonic irradiation. Recently, extensive researches have been conducted on the synthesis of TiO₂ NTs because of their novel properties compared to TiO₂ powder such as high aspect ratio, high surface to volume ratio, high sedimentation rate and versatile chemistry with the conventional advantages and properties of TiO₂ (Menzel *et al.*, 2006; Poudel *et al.*, 2005). The special feature of tubular structure with high aspect ratio provide more opportunities for separation of electron-hole pairs to enhance the electron transfer and improve the interpenetration of holes transport materials due to its delocalization of charge carriers in nanotubes (Menzel *et al.*, 2006; Tachikawa *et al.*, 2006). Thereby, this might help to increase the sonocatalytic degradation efficiency.

MATERIALS AND METHODS

Materials and apparatus: Rhodamine B was purchased from Sigma-Aldrich and was chosen as a model organic compound. Hydrochloric acid, HCl 37%, sodium hydroxide, NaOH (99% purity), tetra-n-butyl-orthotitanate, C₁₆H₃₆O₄Ti or Ti(OBu)₄ for synthesis (≥98% purity), ethanol, CH₃CH₂OH (96% extra purity), hydrogen peroxide solution, H₂O₂ (30% w/w) were obtained from Merck. Potassium hydroxide, KOH (≥98 % purity) was purchased from System Chemical Company. The controllable serial-ultrasonic bath apparatus (Elma Transsonic series TI-H5) was operated to irradiate the aqueous solution of Rhodamine B at a frequency of 35 kHz and effective power output up to 100 W through manual adjusting. A general schematic diagram of experimental scheme is illustrated in Fig. 1. The experimental conditions adopted throughout the whole experiments were initial dyes concentration of 50 and 2000 mg L⁻¹ of TiO₂ amount and neutral initial pH unless other conditions is noted. The concentrations of the samples were determined using Aquamate™ Plus UV-vis spectrophotometer (Thermo Scientific Company) to monitor the degradation of Rhodamine B.

Procedures on catalyst preparation: TiO₂ powder was prepared using the sol-gel and subjected to the heat-treatment. Ti(OBu)₄ was dissolved in ethanol solution with a volume ratio of 4:1 for 1 h under constant stirring. Then, a known quantity of 0.1 M HCl was added to control the pH of solution to prevent the precipitation of TiO₂. The mixture was hydrolyzed at room temperature under stirring for 2 h to obtain a transparent sol. Next, the sol was aged for 2 days at room temperature to obtain a dry gel. The resulting gel was washed with distilled water and dried overnight at 100°C in an oven. After that, the

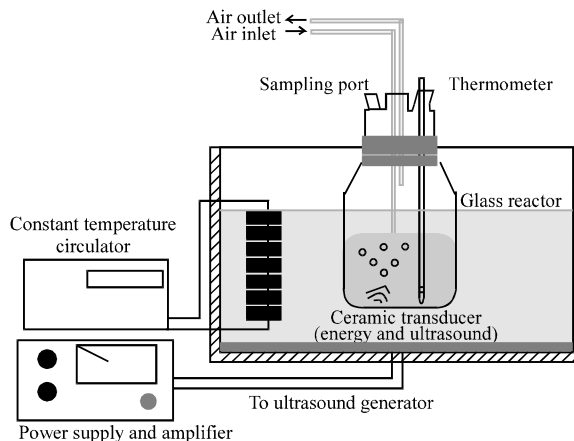


Fig. 1: Schematic illustration of sonocatalytic degradation experiment apparatus

gel powder was calcined at 500°C for 3 h. TiO₂ NTs were synthesized using hydrothermal method which was modified by Bavykin *et al.* (2008). Three gram of synthesized TiO₂ powder was mixed with 98 mL of 10 M NaOH and 2 mL of 10 M KOH solution in a Teflon vessel. The mixture was refluxed at 100°C under stirring for 48 h. The resulted white powder was thoroughly washed with distilled water to remove excess Na⁺ ions. Then, the powder was repeatedly treated with 0.1 M of HCl until the washing solution reached pH 3. Then, it was washed with water before drying it in an oven for several hours at 100°C. Finally, the dried samples were calcined at a temperature of 300°C for 2 h.

Sonocatalytic reaction and analysis of liquid samples:

The prepared 200 mL of Rhodamine B in aqueous solution and TiO₂ powder or NTs were put into the glass reactors. Next, the mixed solution was stirred to make a good dispersion of TiO₂ for 10 min. After that, the mixed solution was put into the ultrasonic bath to ultrasonic treat the organic compound. Lastly, after certain time of ultrasonic irradiation, the liquid samples were centrifuged three times to separate the TiO₂ nanotubes. After that, the liquid sample's concentration was monitored by UV-vis spectrometer to estimate the degradation efficiency concentration of dye solution.

$$\text{Degradation} = \frac{C_0 - C_t}{C_0} \times 100\% \quad (1)$$

Where:

C₀ = Initial dye concentration

C_t = Dye concentration at time t (min)

RESULTS AND DISCUSSION

The UV-vis spectra of Rhodamine B in the presence of TiO₂ NTs and powder: In order to exhibit the degradation of Rhodamine B, the original and degraded Rhodamine B at the interval time of 60 min within 180 min were monitored using UV-visible spectrophotometer in the wavelength of 400 to 800 nm. Figure 2a and b show the UV-visible spectra for the degradation efficiency of Rhodamine B in the presence of TiO₂ powder and TiO₂ NTs, respectively. The maximal absorbency of 40 mg L⁻¹ Rhodamine B solution obeyed by Lambert-Beer's law and the calibration curve of Rhodamine B solutions (figure not shown) were used to estimate the degradation efficiency of Rhodamine B at higher concentration of dye. It was observed that there was only a slightly decreased in the absorbance peak when ultrasonic irradiation using TiO₂ powder was employed after 180 min (Fig. 2a). On the other hand, the absorbance peak of Rhodamine B solutions at 554 nm were decreased sharply along the ultrasonic irradiation time in the presence of TiO₂ NTs. After 180 min of ultrasonic irradiation, the absorbance peak at 554 nm decrease significantly in the presence of TiO₂ NTs as shown in Fig. 2b. The slightly shifted peak from 554 to 550 nm appeared in Fig. 2b is due to the intermediate products formed during ultrasonic irradiation (Wang *et al.*, 2007b). However, the details on the intermediate products forms do not reveal through the absorbance in the UV-vis spectra.

Effect of ultrasonic irradiation time: The effect of ultrasonic irradiation time of the degradation of Rhodamine B was studied under several experimental conditions. The sonolysis of Rhodamine B in the absence of TiO₂ catalyst was act as a control experiment. It was found that the presence of TiO₂ play a significant role in the ultrasonic irradiation. Figure 3 shows that ultrasonic treatment with the presence of TiO₂ had accelerated the degradation efficiency of organic dye. This explanation was supported by Priya and Madras (2006) which claimed that the existence of particles in liquid would provide a nucleation site for cavities formation due to its surface roughness. This may increase the dissociation of H₂O molecules to form more •OH radicals which are highly reactive and therefore short-lived.

Meanwhile, it was observed that Rhodamine B degraded faster in the presence of TiO₂ NTs (85%) than TiO₂ powder (25%). This could be attributed to its higher specific surface area and porosity characteristic which provide more nucleation sites for cavitation bubble formation as compared to TiO₂ powder. Besides, the inner and outer surfaces of TiO₂ Nts could increase, which

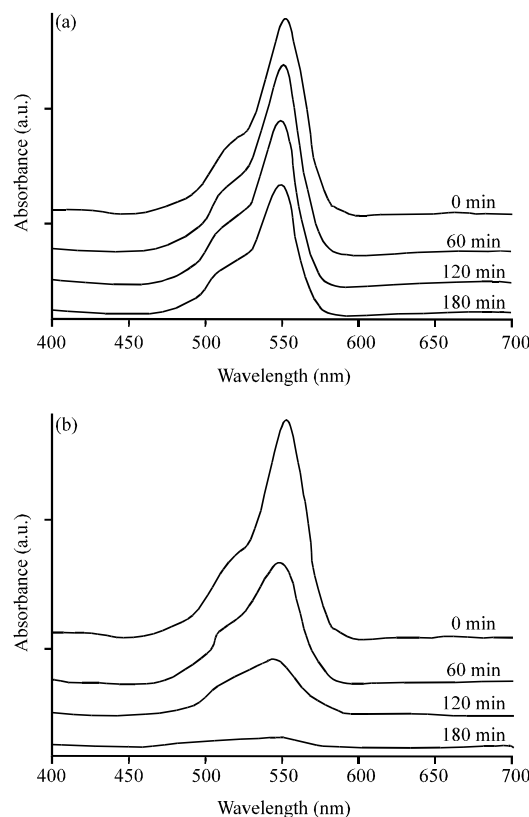


Fig. 2: UV-vis spectra of Rhodamine B solution in the presence of (a) TiO₂ powder and (b) TiO₂ Nts

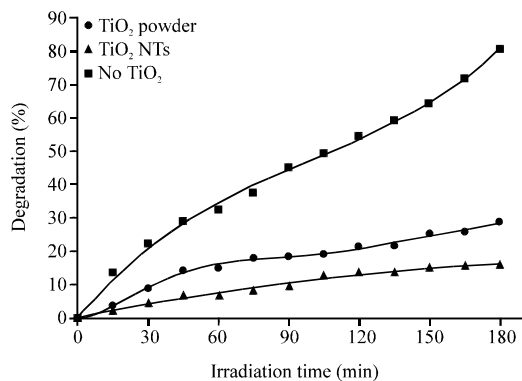


Fig. 3: Effect of irradiation time on the sonocatalytic degradation of Rhodamine B. (Initial dye concentration = 50 mg L⁻¹, catalyst loading = 2.0 g L⁻¹, solution temperature = 30°C)

resulted in more surfaces available to restrain the recombination of electron-hole pairs. Tachikawa *et al.* (2006) reported that TiO₂ in the form of NTs.

Could increase of delocalization of charge carriers in nanotubes where the separated electrons and holes were

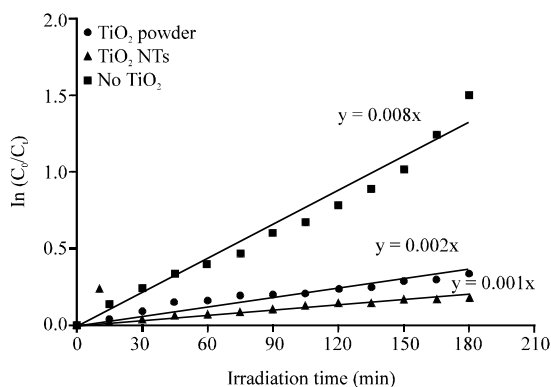


Fig. 4: The reaction kinetics plot for the sonocatalytic degradation of Rhodamine B

free to move throughout the length of the crystal in order to reduce the recombination probability. These holes not only can decompose the organic dyes adsorbed on the surface of TiO₂ particles directly, but also could accelerate the generation of •OH radicals through oxidizing H₂O molecules in the bulk solution (Wang *et al.*, 2007b).

In addition, the degradation kinetics of Rhodamine B in aqueous solution by using ultrasonic irradiation with and without TiO₂ NTs or TiO₂ powder was investigated. As shown in Fig. 4, the results are presented in the form of a plot of ln(C₀/C_t) as a function of irradiation time (t) indicated that the degradation of Rhodamine B satisfactory followed a pseudo-first-order kinetics. The pseudo-first-order rate constant, k values and corresponding regression coefficients (R²) under various operational conditions are listed in Table 1. It was observed that there was a double increased in k value when ultrasonic was applied in the presence of TiO₂ as compared to the control experiment (without TiO₂). Again, it was clearly shown that k value for the case of ultrasonic irradiation in the presence of TiO₂ NTs was significant higher than in the presence of TiO₂ powder. This implied that the degradation rate of Rhodamine B was higher and could achieve higher degradation efficiency in a shorter time. Similar degradation kinetic for reported for the photocatalytic degradation (Grzechulska and Morawski, 2002) and sonocatalytic degradation of organic dyes (Abdullah and Ling, 2010; Abbasi and Asl, 2008).

Effect of initial dye concentration: Initial concentrations of Rhodamine B solution ranging from 50 to 150 mg L⁻¹ were used to review the effect of initial dye concentration on the degradation efficiency of Rhodamine B. Results from Fig. 5 shows that the degradation efficiency decreased with the increasing of initial dye concentration in the presence of either TiO₂ powder or TiO₂ NTs. In this

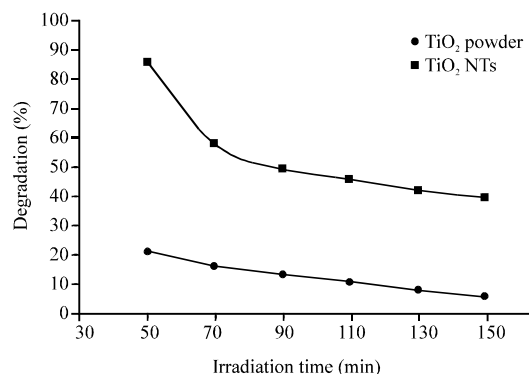


Fig. 5: Effect of initial dye concentration on the sonocatalytic degradation of Rhodamine B. (Catalyst loading = 2 g L⁻¹, solution temperature = 30°C, reaction time = 180 min)

Table 1: Rate coefficients for the sonocatalytic degradation of Rhodamine B under various conditions

Experiment condition	k _{app} (min ⁻¹)	r ²
US + TiO ₂ NTs	0.008	0.941
US + TiO ₂ powder	0.002	0.897
US only	0.001	0.946

respect, the sonocatalytic degradation process showed some similarities with those of a photocatalytic process (Grzechulska and Morawski, 2002; Harir *et al.*, 2009). This might be due to the excessive adsorption of the Rhodamine B molecules on the surface of TiO₂ until it was fully covered the surface of TiO₂. Besides, when increasing the initial dye concentration, the mutual screens between Rhodamine B molecules and TiO₂ increased too. These two phenomena would prohibit TiO₂ from absorbing heat and energy resulting from the acoustic cavitation and also disturbed the transmission of ultrasound. Thus, this would limit the •OH radicals that could attack certain dye molecules and leading to decrease in the degradation efficiency.

Effect of TiO₂ loading: In order to optimize the addition amount of TiO₂ catalyst to achieve highest sonocatalytic degradation efficiency, the addition amount starting from 500 to 3000 mg L⁻¹ were adopted. Results from Fig. 6 show that the degradation efficiency of Rhodamine B rised sharply when the addition amount of TiO₂ NTs increased from 500 to 2500 mg L⁻¹. It began to decline after addition amount was increased to 3000 mg L⁻¹ and further. Similar trend occurred when using TiO₂ powder. This phenomenon can be explained by the fact that the excessive TiO₂ particles caused TiO₂ particles to come nearness and aggregation. This would result the decreasing number of surface active sites at TiO₂. In

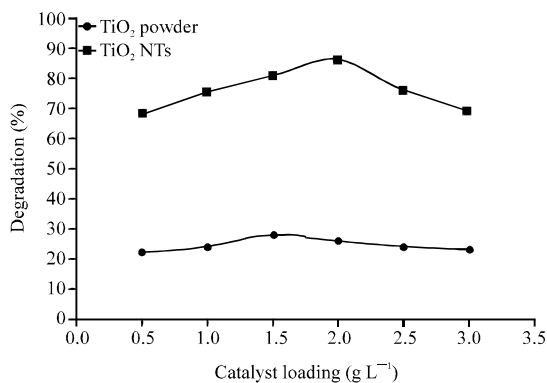


Fig. 6: Effect of catalyst loading on the sonocatalytic degradation of Rhodamine B. (Initial dye concentration = 50 mg L⁻¹, solution temperature = 30°C, reaction time = 180 min)

addition, mutual screens among TiO₂ increased that would make the Rhodamine B molecules received extra protection. Then, it would prohibit TiO₂ from absorbing heat and energy resulting from the acoustic cavitation (Abdullah and Ling, 2010). Consequently, it might result in a small chance that dye molecules encountered •OH radicals produced by ultrasound. Such a phenomenon was not observed in this study. The amount of TiO₂ NTs required (2000 mg L⁻¹) to achieve highest sonocatalytic degradation efficiency was found more than the amount of TiO₂ powder (1500 mg L⁻¹). The different optimal catalyst adding amount for TiO₂ NTs and TiO₂ powder was generally depended on the nature of the catalyst, organic pollutant and other many factors (Wang *et al.*, 2006a).

Effect of the solution temperature: The effect of aqueous temperature ranges from 20 to 70°C on the sonochemical reaction rate were investigated at ultrasonic frequency of 35 kHz with an ultrasonic power of 50 W. Figure 7 shows that as the solution temperature increased from 20 to 70°C, degradation rate of Rhodamine B decreased sharply and slowly in the presence of TiO₂ Nts and powder, respectively. Similar decreasing trend had been reported by Jiang *et al.* (2006) and Wang *et al.* (2006a) on the sonocatalytic degradation of 4-chlorophenol and methyl parathion, respectively. It was reported that an increase in temperature will lead to an increase in the possibility of coalescence among the cavitation bubbles, resulting in some of the bubbles losing their activity (Jiang *et al.*, 2006).

Besides, the tiny cavitation bubbles would volatilize from the solution before growing and collapsing under ultrasonic irradiation when increasing the solution temperature (Wang *et al.*, 2006a). Another reason was due the fact that high temperature would prohibit the

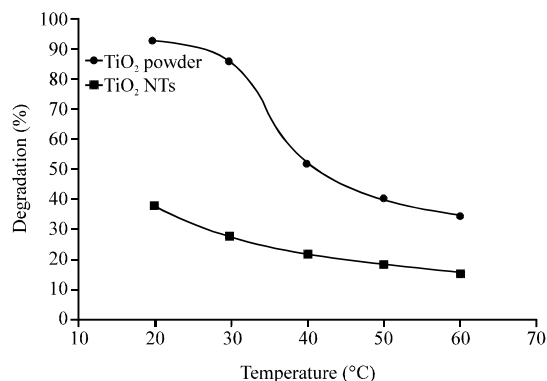


Fig. 7: Effect of solution temperature on the sonocatalytic degradation of Rhodamine B. (Initial dye concentration = 50 mg L⁻¹, TiO₂ NTs = 2 g L⁻¹ or TiO₂ powder = 1.5 g L⁻¹, reaction time = 180 min)

absorbability of organic dyes on the surface of TiO₂. The proper quantities of organic dyes adsorbed on the surface of TiO₂ catalyst can directly decomposed by the holes (Wang *et al.*, 2006b). These entire phenomenons would decrease the degradation efficiency as the solution temperature was increased. Higher degradation efficiency was obtained at lowest solution temperature but it was tough to maintain its low temperature for longer irradiation time. Thus, the room solution temperature was chosen for our next study.

Effect of addition of H₂O₂: The sonocatalytic degradation of Rhodamine B in the presence of either TiO₂ NTs or powder was studied for comparison of the different addition amount of H₂O₂ ranges between 4 to 16 mM. From Fig. 8, it was found that the degradation rate of Rhodamine B in the presence of either TiO₂ powder or TiO₂ NTs increased when H₂O₂ concentration was increased up to 8 mM but at higher levels, there was a drop in the degradation rate. Similar trend of results were reported for sonocatalytic degradation of Congo Red (Abdullah and Ling, 2010), Methylene Blue (Abbasi and Asl, 2008; Shimizu *et al.*, 2007) and photocatalytic degradation of organic pollutant (Harir *et al.*, 2009) in the presence of TiO₂ and H₂O₂. The addition of H₂O₂ below 8 mM could increase the formation rate of •OH radicals in two ways. Firstly, the reduction of H₂O₂ at the conduction band (Eq. 2) and secondly was the self-decomposition of H₂O₂ to produce more •OH radicals (Eq. 3) (Abbasi and Asl, 2008). This could enhance the degradation rate of Rhodamine B in aqueous solution. Another reason might be due to relatively easier decomposition of into •OH radicals under ultrasonic irradiation as the dissociation energy for the O-O bond in H₂O₂ is 210 kJ mol⁻¹ which is

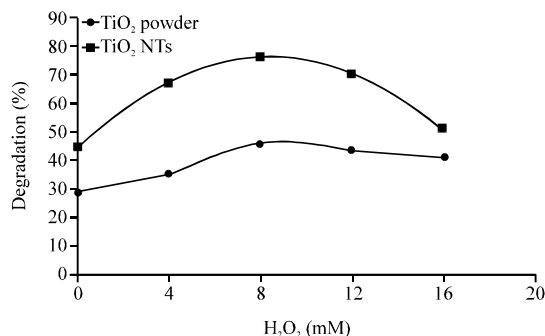
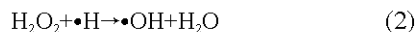


Fig. 8: Effect of the added amount H₂O₂ on the sonocatalytic degradation of Rhodamine B. (Initial dye concentration = 50 mg L⁻¹, TiO₂ NTs = 2 g L⁻¹ or TiO₂ powder = 1.5 g L⁻¹, solution temperature = 30°C, reaction time = 120 min)

less than that of the O-H bond in H₂O that is 4663 kJ mol⁻¹ (Wang *et al.*, 2008a).



It is a fact that H₂O₂ molecule could act as a hydroxyl source as well as hydroxyl scavenger under sonocatalytic condition (Abdullah and Ling, 2010). Thus, at higher concentration of H₂O₂ (above 8 mM), the surplus •OH radicals produced from the dissociation of H₂O₂ might undergo 3 pathways: react with H₂O₂ and produce less reactive species hydroperoxyl (•OOH) radicals, react with •OOH radicals to form H₂O and self-recombination back to form H₂O₂ (Minero *et al.*, 2005). This could inhibit the production of valence bond holes and •OH radicals that able to cause less organic dye to be degraded.

Effect of the presence of air flow: In order to investigate the effect of dissolved air, four experiments were performed in the absence and presence of air bubbling in the Rhodamine B solution. For all these experiments run, the degradation of Rhodamine B increases with the use of 1 L min⁻¹ of air flow as shown in Fig. 9. This result indicated that the sonocatalytic degradation of Rhodamine B in the presence of H₂O₂ enhanced as a result of addition of air flow to the solution. The sonocatalytic degradation Rhodamine B using TiO₂ NTs with the presence of air increased from 76 to 85%. Similar trend appeared on the degradation when using TiO₂ powder as sonocatalyst which increased from 43 to 53%. The increasing degradation rate with the supply of air flow

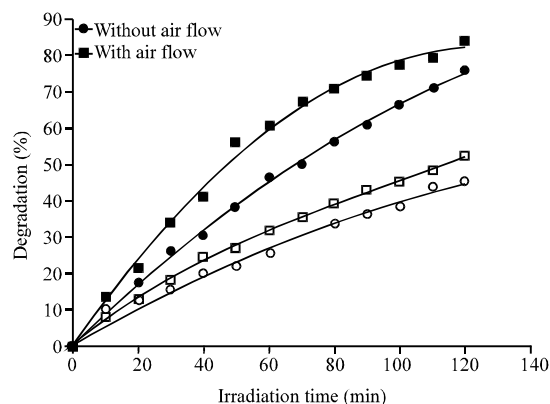


Fig. 9: Effect of the presence of air flow on the sonocatalytic degradation of Rhodamine B. Filled and open symbols indicated TiO₂ NTs and TiO₂ powder, respectively. (Initial dye concentration = 50 mg L⁻¹, TiO₂ NTs = 2 g L⁻¹ or TiO₂ powder = 1.5 g L⁻¹, solution temperature = 30°C, [H₂O₂]₀ = 8 mM)

into the solution might be due to the production of •OH and other radicals such as •NO₂ and •NO₃. Some of the radicals formation that might take place during injection of air into Rhodamine B solutions have been reported by Inoue *et al.* (2006) and Kidak and Ince (2006). Goel *et al.* (2004) reported that 10% of these reactive radicals generated in the cavitation bubbles could diffuse into the bulk solution. Then, the degradation rate of Rhodamine B could increase as non-volatile organic (Rhodamine B) was mostly attacked by •OH radicals in the region of bulk solution and interface bubble-water (Goel *et al.*, 2004; Kidak and Ince, 2006).

CONCLUSIONS

In the present study, it was found that TiO₂ NTs had better degradation effect than TiO₂ powder in sonocatalytic activity. The highest sonocatalytic degradation efficiency for Rhodamine B (85% within 120 min) occurred at 50 mg L⁻¹ initial concentration of dye with concentration of TiO₂ NTs at 2000 mg L⁻¹, concentration of H₂O₂ at 8 mM, ultrasonic power of 50 W, ultrasonic frequency of 35 kHz, air flow rate of 1 L min⁻¹ and neutral pH at room temperature. Hence, TiO₂ NTs material was proven as a highly potential environmental catalyst and can become an alternative choice for large-scale applications for ultrasonic irradiation.

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