Decoloration of Rhodamine B Aqueous Solution by Ultrasound Assisted Pulse Discharge

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Abstract: Research on the decoloration of refractory dye, Rhodamine B (RhB) by ultrasound assisted pulse discharge process has been carried out. The effects of ultrasound on the pulse discharge type, decoloration rate and energy efficiency of pulse discharge were investigated in various electrical conductivity of the solution. The proposed technique extends the treatable range of solution electric conductivity and shows a significant improvement on RhB decoloration, and the energy efficiency of pulse discharge was promoted. In addition, the RhB decoloration in the presence of H_2O_2 was studied. Results show that RhB decoloration has been inhibited by additive H_2O_2.

1 INTRODUCTION

Wastewater from textile, food, leather, pharmaceutical, and paper industries are one of the major water pollutant sources. Finding efficient methods to disposal those colored wastewaters has become an important issue for environmental protection as well as those industries (Lee et al., 2013). Rhodamine B (RhB) is a highly water soluble refractory organic compound, which is a widely used xanthene dye for industry purposes. It is harmful to animals and human beings, which would cause irritation to eyes, skin and respiratory tract. (Merouani et al., 2010). Conventional methods to remove RhB and similar refractory dye pollutant are absorptions on activated carbon, reverse osmosis or coagulation by chemical agents. However, those non-destructive methods can hardly eliminate the threat of RhB to environment (Behnajady et al., 2008).

In recent years, advanced oxidation processes (AOPs) have been widely investigated as a promising method for organic pollutant removal(Siddique et al., 2014, Liang et al., 2007). Pulse discharge, one of major AOPs, shows great potential in pollutant removal, especially the refractory organic compounds pollutant (Van de Moortel et al., 2017). By inducing high energy into reaction zone in a short time, generation of radicals (·OH, O·, and HO_2·), shock waves, UV irradiation and direct pyrolysis of pollutant could be achieved. Degradation efficiency of RhB by ·OH radical attack has been proved in pulse discharge process(Sugiarto et al., 2003). However, conventional pulse discharge in liquid requires much higher input voltage than that in air. In addition, liquid discharge is also very sensitive to the environment. High solution conductivity leads to discharge type change from spark type to streamer type, which shows undesirable decoloration efficiency on RhB (Nakagawa et al., 2003).

Ultrasound has also been investigated as an AOP for wastewater treatment. Ultrasound irradiation induces generation of numerous cavitation bubbles in which it is transmitted. After the nucleation and compression-refractions cycles, those microbubbles collapse when they reach a critical size(Fang et al., 2018a). High temperature (6000K) and pressure (1000atm) of bubble collapse in the small volume induces the generation of radicals. Moreover, the diameter of cavitation bubbles usually lies in the range of tens of microns. Recent research shows that micrometer scale bubbles in water can help generate spark type discharge with a lower input voltage (Bruggeman and Leys, 2009, Medodovic and Locke, 2009). Therefore, it is a promising approach to utilize cavitation bubbles to obtain desirable spark discharge, consequently, higher pollutant removal efficiency.

In this research, a new technique which combines pulse discharge and ultrasound is proposed to enhance the decoloration of RhB. This research

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focuses on the assistance of cavitation bubbles on pulse discharge in liquid. To achieve this goal, test on effects of ultrasound on discharge type was performed firstly, and then RhB decoloration experiments were carried out by ultrasound, pulse discharge and ultrasound assisted pulse discharge respectively. In addition, the effects of irradiative H_2O_2 solution were also investigated.

2 EXPERIMENTAL SETUP AND METHODOLOGY

The experimental setup, as shown in Figure 1, consists of an ultrasound generation system, main reactor, pulse generation circuit, an electrical analytical system and cooling device. An ultrasound generator (TELSONIC, Switzerland) with adjustable vibration amplitude was applied to irradiate ultrasound waves at a frequency of 20 kHz into a water bath through a sonotrode connected with a piezoceramic transducer. The peak-to-peak amplitude of the sonotrode tip was ranged from 40 to 75 μm (p-p). Notice that the threshold vibration amplitude exceeding which causes developed cavitation in water is 4~5 μm (p-p)(Komarov et al., 2013). The reactor comprises of a cylindrical sonotrode (Diam. 48 mm), a needle shape high voltage electrode made of tungsten wire (Diam. 1 mm), and a cylindrical vessel (Diam. 140 mm, height 190 mm) made of acrylic resin. The sonotrode is composed of two cylindrical parts, one is made of ceramic to prevent the ultrasound generator from high voltage damage, and the other one is made of titanium serving as the sonotrode tip and grounded electrode. Dimensions of both parts were adjusted to resonance conditions. The distance between electrodes is an important parameter influencing the pulse discharge efficiency. In this research, the distance was set to 4 mm according to preliminary experiments in optimizing the performance of spark type discharge unit.

Pulse generation circuit is showed by the blue line. A DC power supply (0~+40 kV) was used to charge a capacitor (1000 pF), and then it was discharged into the reactor through a spark gap discharge unit. Voltage and current signals between the electrode during the plasma discharge were collected by an oscilloscope through a 1000:1 reduction ratio high voltage probe (PINTEC, China) and a coil current probe (IWATSU, Japan) respectively. A water-cooling coil was submerged in the reactor to maintain the water temperature at a level of 20±2 ºC.

High purity RhB was purchased, and 5 mg/L RhB concentrations solutions were prepared using distilled water. H_2O_2 solution (500ml) with 30% concentration was purchased from Wako, Japan. Each experiment of RhB degradation lasted for 12 minutes, and solution samples were taken each 3 minutes. RhB concentration was determined from the absorbance measured by a spectrophotometer (AS-ONE ASV11D, Japan) at 554 nm wavelength. After the treatment, the decoloration rate ξ and energy efficiency η was calculated as follows:

$$\xi = \frac{\Delta[RhB]}{[RhB]_0}$$

$$\eta = \frac{V\Delta[RhB]}{EfT}$$

where $[RhB]_0$is the initial RhB concentration, V is the solution volume, $\Delta[RhB]$ is the concentration change of RhB, E is the energy of fully a charged capacitor, f is the pulse discharge frequency, T is the treatment time.

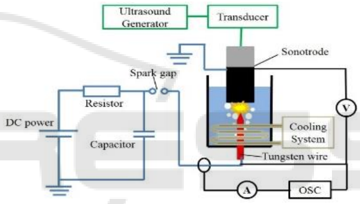

Figure 1: Sketch of the experimental setup.

In this research, the output voltage was 25 kV, pH was about 5 (RhB aqueous solution without any acid or alkaline addition). The solution conductivity was adjusted using a NaCl solution.

3 RESULTS AND DISCUSSION

3.1 Effects of Ultrasound on Pulse Discharge Type

Pulse discharge type plays a vital role in liquid discharge technique for pollutant removal, especially for refractory organic pollutants (Sugiarto and Sato, 2001). In the proposed process, the electrodes, which comprises a tungsten wire and sonotrode, can be regarded an as a needle-plate electrode arrangement. Moreover, in a needle-plate pulse liquid discharge system, discharge type can be varied into spark discharge, streamer discharge and mixing discharge (spark and streamer discharge type). These discharge types mainly concerned with the output voltage of the power supply, distance between electrodes, electric conductivity of solution and the pressure. In this research, the output voltage, electrode distance, and pressure were fixed. Thus, electric conductivity was considered as the only factor to discharge type changes.

Spark discharge usually appears as a single plasma channel between electrodes with high energy density. The formation of this plasma channel induces strong electron clusters, UV irradiation, and shock waves into liquid around the channel, which remarkably promotes exciting ionizing water molecular. Consequently, the generation of radicals is improved.

In the case of streamer discharge, it has many intense but weak channels growing from one electrode (usually from a needle electrode in needle-plate system). Streamer discharge generates higher pulse current and stronger UV light than spark discharge. However, the low energy density of streamer discharge induced limit ionization and excitation gives low radicals yield(Medodovic and Locke, 2009).

Mixing discharge type in this research means a combination discharge type (spark discharge and streamer discharge), that long plasma channel between electrodes and short, intense channels exist at the same time. These channels are more stretched than in the other cases. This discharge type gives the best degradation efficiency on phenol than spark and streamer type, presented by Sugiarto (Sugiarto and Sato, 2001).

In this research, Table 1 shows the discharge type changes of pulse discharge and ultrasound assisted pulse discharge in various electric conductivity. This test was carried out with an electric conductivity range of 5~1000 µS/cm. Different discharge types can be identified with digital data from oscilloscope and observation. For solely pulse discharge, spark and mixing discharge, which is believed to be effective in pollutant removal, was limited in 5~70 µS/cm, while for ultrasound assisted pulse discharge process, it was remarkably expanded to 1000 µS/cm, almost increased by 13 times.

With the assistance of ultrasound, numerous cavitation microbubbles were generated between electrodes, which help decrease the breakdown threshold and help plasma propagate through the gas phase inside bubbles. Bubble surface takes an important role in pulse discharge. When applying an electric field on a liquid-gas phase, the charge will accumulate on the surface of bubbles (Gershman et al., 2007, Yamabe et al., 2005). Due to the huge bubble surface of numerous cavitation bubbles, the discharge will be generated through bubbles instead of water medium, and a spark type discharge can be achieved even in higher electrical conductivity solution.

Table 1: Discharge type changes of P (pulse discharge) and UP (ultrasound assisted pulse discharge) in various ranges of electric conductivity of solution (/µS·cm^{-1}).

	5~30	30~70	70~1000
P	Spark	Mixing	Streamer
UP	Spark	Spark	Mixing

3.2 Effects of Ultrasound Assistance on RhB Decoloration

Decoloration tests of RhB were carried out to evaluate the performance of the proposed process. Due to the decomposition of RhB molecular, the electric conductivity of solution will continuously increase. To avoid discharge type changing caused by electric conductivity, the decoloration tests were limited in 12 minutes, with an average of 10 µS/cm growth in electric conductivity.

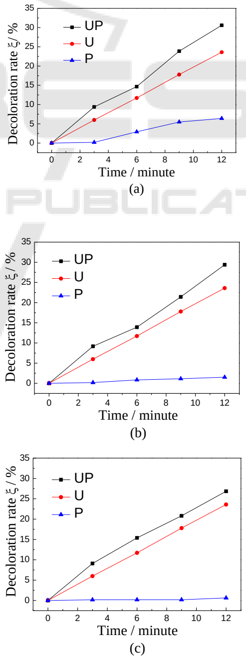

Figure 2: RhB decoloration rate of various methods (UP: ultrasound assisted pulse discharge. U: ultrasound singly. P: pulse discharge singly) in (a) 20, (b) 60 and (c) 200 µS/cm solutions.

Figure 2 shows the effects of ultrasound assistance on RhB decoloration in various electric conductivity solutions. Treatments by ultrasound and pulse discharge singly were also investigated for comparisons. Ultrasound assisted pulse discharge gives the highest decoloration rate rather than another two approaches, and the decoloration slightly decreases in a higher electrical conductivity solution. No significant effects of electrical conductivity can be found on the decoloration by ultrasound singly, while the decoloration rate almost decreases to zero when conductivity above 60 µS/cm. In 20 µS/cm solution, it will cost much energy to breakdown water medium. When solution conductivity increase, pulse discharge type usually transfers from spark type to streamer type, which has more intense plasma channels but low energy density (Šunka, 2001). In this case, much energy was consumed into current heat instead of RhB decomposition. The sole ultrasound gives relatively high decoloration rate even the amplitude was set at 40 µm (p-p), the minimum of an ultrasound generator. This is because even with the minimum amplitude of sonotrode, a strong cavitation field could be generated, and caused effective decomposition of RhB molecular.

In addition, irradiation of ultrasound in liquid will cause a macro steady flow due to the soundwave attenuation in water medium, named acoustic streaming, which helps improve the mass transfer in reactor, consequently yield a better decoloration rate (Fang et al., 2018b).

Table 2 shows the data of energy efficiency of each approach. $\eta_{p'}$ is the mean energy efficiency of improved pulse discharge by ultrasound, which was calculated as follows:

$$\eta_{P'} = \eta_{UP} - \eta_U$$

Where η_{UP} is energy efficiency of ultrasound assisted pulse discharge, η_U is the energy efficiency of ultrasound. It can be found that in energy efficiency of pulse discharge was significantly improved by ultrasound, especially in higher electrical conductivity solution.As discussed in previous part, the existence of cavitation bubbles between electrodes help plasma to propagate in the gas phase inside bubbles, thus more energy could be used for RhB decoloration. Moreover, discharge types in 60 and 200 µS/cm solution were changed by cavitation bubbles to spark discharge and mixing discharge respectively. Spark discharge and mixing discharge give a much higher radical yield, and induce extreme physical conditions (strong shock wave and 3000~5000K high temprature), which improve the decoloration of RhB. While for streamer discharge, much energy was consumed into current heat, consequently decreased energy efficiency. Compare with other liquid discharge process for dye decoloration (Malik, 2010), especially for those RhB decoloration researches, ultrasound assisted pulse discharge shows a promising energy efficiency, such as Anto presented 0.081 g/kWh for spark discharge and 0.025 g/kWh for streamer discharge (Sugiarto et al., 2003).

Table 2: Energy efficiency η (g/kWh) in P (solely pulse discharge) and P' (improved pulse discharge) with different solution electrical conductivities.

	20 µS/cm	60 µS/cm	200 µS/cm
P	0.191	0.048	0.013
P'	0.267	0.257	0.107

3.3 Effects of Additive H_2O_2 Solution

H_2O_2 is a commonly used method to combine with AOP process to help generate radicals to decompose pollutants (Mehrdad and Hashemzadeh, 2010, Mehrdad et al., 2011). In this part, effects of different concentrations of H_2O_2 were investigated with ultrasound assisted pulse discharge method. The result is shown in Figure 3.

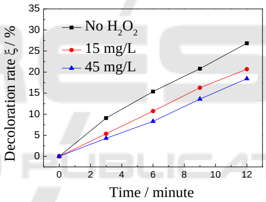

Figure 3: RhB decoloration rate as a function time of time with various concentrations of H_2O_2.

It is clear that the decoloration rate decreases in higher H_2O_2 concentration. Similar results have been reported in related researches (Behnajady et al., 2008, Merouani et al., 2010). However, in these researches decreasing trend of RhB decoloration appears after a relatively large dosage of the additive H_2O_2 solution.

It is known that solely H_2O_2 solution shows very limit decoloration on RhB. OH radical is mainly responsible for RhB decoloration of those AOPs techniques. In this research, because of the short life time and diffusion distance of OH radicals, decoloration reaction is mainly conducted on the interface between liquid phase and gas phase (induced by cavitation and plasma evaporation). However, H_2O_2 would also take part of the interface, after reaching a certain saturation limit, there would be no enough interface area for the decoloration reaction. The acoustic streaming will also improve

H_2O_2 diffusion to the interface. Consequently, the decoloration rate was decreased. On the other hand, due to a large amount of ·OH radical generated in proposed process, more OH radicals were scavenged by H_2O_2 instead of attacking RhB molecular. The inhibitory effect of H_2O_2 could be explained as follows:

$$H_2O_2 + \cdot OH \rightarrow H_2O + HOO\cdot$$

In this case, the scavenging effect of H_2O_2 shows more influences rather than releasing ·OH radical. Thus, the decoloration will decrease with the increasing additive H_2O_2.

4 CONCLUSIONS

The present work has shown that RhB can be effectively removed from aqueous solution by proposed ultrasound assisted pulse discharge. Solution electrical conductivity for desirable discharge type is widely extended. Energy efficiency of discharge is significantly improved by ultrasound, especially in higher electrical conductivity of solution. Additive H_2O_2 solution shows an inhibitive effect on RhB decoloration in proposed method. Additive H_2O_2 performs as a inhibitor in the experiments.

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