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Degradation of methylene blue in micro-bubbles activated sodium persulfate system

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Abstract. To better understand the promoting effect of the activation process, the performance of micro-bubbles for sodium persulfate activation was evaluated in this study. The degradation rate reached to 91.3% at 90th min in the micro-bubbles activated reactor (MAR), whereas reached to 85.7% at 250th min in the high temperature activated reactor (HTAR). Based on the fitted models, it can be indicated that the reaction rate constant was 2.45 times in the micro-bubbles activated reactor than that in the high temperature activated reactor. It can be concluded that micro-bubbles can effectively strengthen the activation process of sodium persulfate.

1. Introduction

Currently, there are approximately 30,000 kinds of dyes were used, and 600,000 tons dyes are discharged into the environment has reached per year in the world, which causes a great challenge for the ecological environment governance [1]. Approximately one million tons dyeing wastewater are produced per year all over the world, more than 10 percent of which are discharged directly into the environment [2]. Wastewater from dye house features low biodegradability, large chroma and complex compositions, which has become a serious problem on the environment. Currently, biochemical, physical and chemical treatment methods have been adopted to treat dyeing wastewater.

Advanced oxidation technology, which was widely used in dyeing wastewater treatment, has the advantages of high efficiency, fast response, and low pollution. Some researchers have shown that strong oxidizing radicals can be produced by photoactivation, thermal, transitional metals, and so on. Unlike conventional bubbles, micro-bubbles' average diameter is less than 50 nm. In pure water, the surface of the micro-bubbles has ζ potential, and the average value is approximately -35 mV. Due to high inner pressure, micro-bubbles will shrink and collapse beneath the water surface [3-5]. Previous work has shown that free radicals can be generated by the collapse of micro-bubbles without dynamic stimulus [6]. Moreover, hydroxyl radicals with higher standard redox potential have shown immediate reactivity with the majority of organic compounds. Therefore, the micro-bubble technology was introduced to the activation process of the sodium persulfate [7].

In this study, the performances of MAR and HTAR were compared to investigate the mechanism of activation process. The objectives of this paper were to observe the reaction rate of activation process with micro-bubbles. In addition, some informations can be provided in this paper to improve the advanced oxidation technology in the next step [8].



2. Materials and Methods

2.1. Material Sources

Methylene blue is an alkaline dye with chemical formula of $C_{20}H_{15}N_2S_2O_7Na_2$, and its most proper absorption wavelength is 664 nm. Dye wastewater was prepared by dissolving methylene blue, and the solution concentration was $20 \text{ mg} \cdot \text{L}^{-1}$.

2.2. Test Instruments

A schematic diagram of the experimental device is shown in Figure. 1. The experimental system includes three parts: a water bath system, a reactor and a diffuser device. The air flow range of the micro-bubbles generator was $0.2 \text{ L} \cdot \text{min}^{-1}$. A laboratory-scale reactor with an internal diameter of 350 mm and a working volume of 4 L was fabricated by Plexiglas glass. The hydraulic retention time (HRT) is 250 min

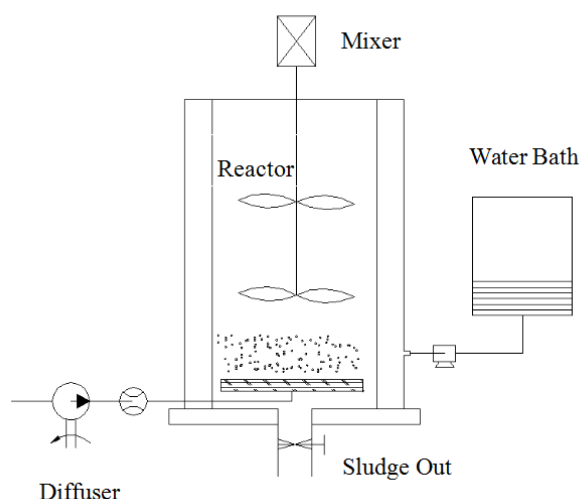


Figure 1. Schematic diagram of the experimental equipment.

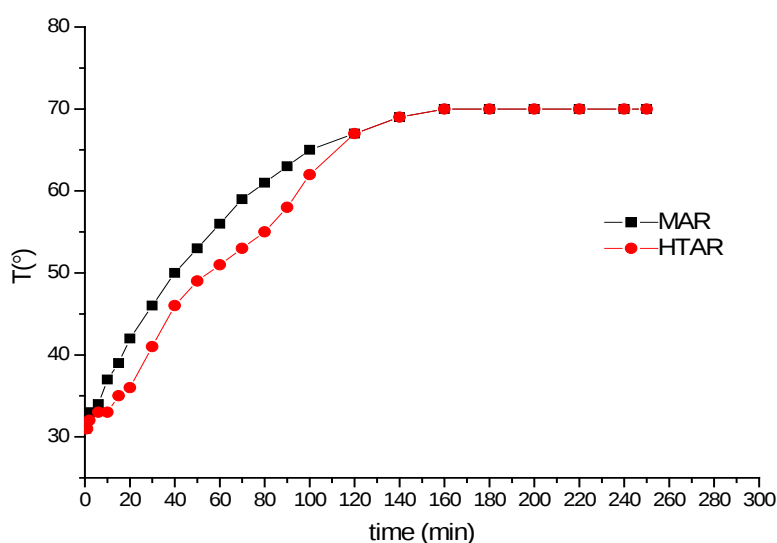


Figure 2. The temperature change during the reaction.

The micro-bubbles generator was introduced in the micro-bubbles activation reactor, and the gas flow was controlled at $0.2 \text{ L} \cdot \text{min}^{-1}$ to produce more micro-bubbles. As shown in Figure. 2, the temperature was increased with the generation of micro-bubbles. The temperature in the HTAR were controlled the same with that in the MAR by the water bath system.

2.3. Analysis Method.

Thermometers were used to measure the temperature in the reactor. The concentration of methylene blue was measured by UV spectrometry. UV-Vis spectroscopy was performed with a Shimadzu UV-1700 PC spectrophotometer within the range of 190-500 nm [9].

3. Results and Discussion

3.1. Concentrations of Methylene Blue

As shown in Figure. 3, the concentrations of methylene blue gradually decreased both in the MAR and HTAR, and chroma finally reached to a clear liquid with increasing reaction times. The degradation rate reached to 91.3% at 90th min in the MAR, whereas reached to 85.7% at 250th min in the HTAR. At the 250th min, the concentrations of methylene blue decreased from $20.00 \text{ mg} \cdot \text{L}^{-1}$ to $0.07 \text{ mg} \cdot \text{L}^{-1}$ in the MAR, and to $0.53 \text{ mg} \cdot \text{L}^{-1}$ in the HTAR. This means methylene blue was degraded more thoroughly in micro-bubbles activated sodium persulfate system. This phenomenon indicated that the micro-bubbles was benefit for the degradation of methylene blue, as well as the activation process of sodium persulfate[10].

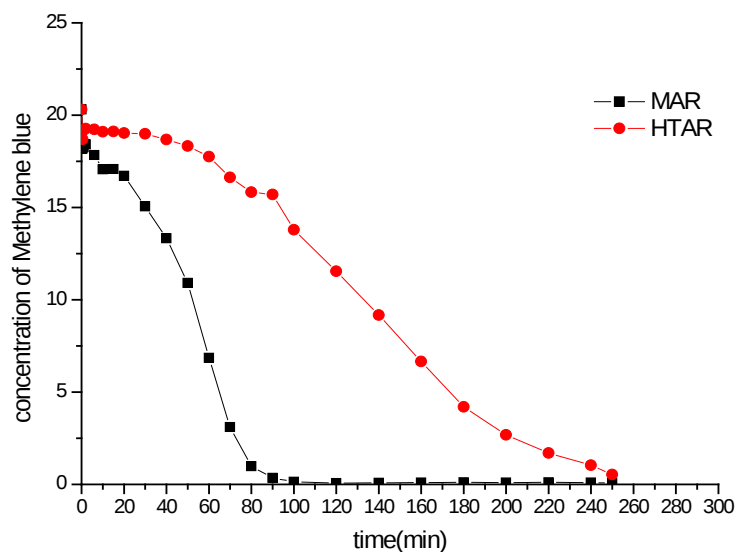


Figure 3. Changes in the concentrations of methylene blue during the reaction processes.

3.2. The First-Order Kinetic Model Fitting

According to Figure. 3, experimental data showed that the first order model fitted the reaction more. And the original first-order kinetics reaction equation for $E_t = E_z(1 - e^{-kt})$, in which

$$E_t = \frac{c_0 - c_t}{c_0} \quad (1)$$

where c_0 is the concentration of methylene blue at initial moment, c_t is the concentration of methylene blue at t moment, E_t is the decolorization rate at t moment, E_z is the decolorization rate at equilibrium moment, and k is the methylene blue degradation reaction rate constant.

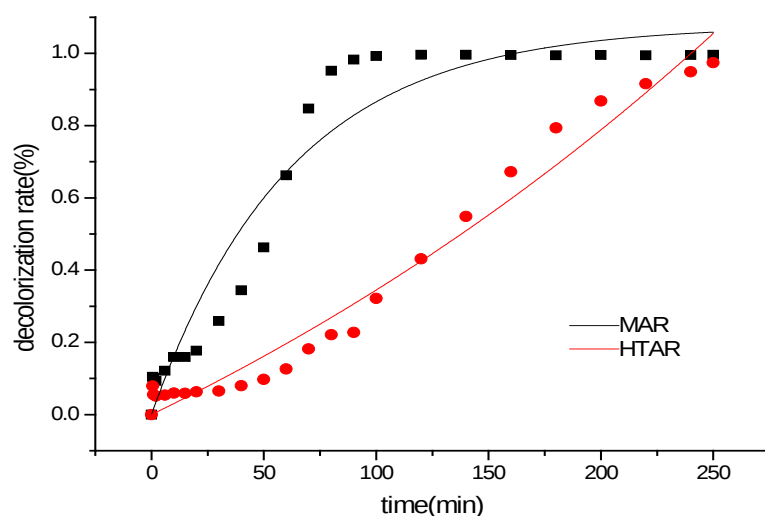


Figure 4. Degradation models for decolorization rate of methylene blue.

As shown in Figure. 4, the correlation coefficient of 0.97, 0.94 showed that the experimental data agree well with the model. The reaction rate constant showed a distinct difference between the HTAR and the MAR, and the reaction rate constant was 0.0025 and 0.0163, respectively. In addition, the reaction rate constant in the MAR is 6.52 times than that in the HTAR. This is more direct evidence that proved the advantages of micro-bubbles activation in the degradation of methylene blue wastewater using activated sodium persulfate.

3.3. Mechanism Analysis

Micro-bubbles have a high inner pressure, resulting in the shrinkage and collapse of the micro-bubble under water [11]. Some researchers have shown that the micro-bubbles collapse also results in the decomposition of refractory organic compounds [12]. Previous work has provided evidence that, even in the absence of a dynamic stimulus, free radicals still can be produced by the collapse of micro-bubbles, thus increasing the number of free radicals in the solution [13]. Because radicals have a higher standard redox potential and show immediate reaction activity with most organic compounds, the application of micro-bubble technology to is considered to improve the activation process of sodium persulfate[14].

Second, micro-bubbles generator titanium porous diffuser was cylindrical with a pore size of 45 μm [15]. The mean diameter of the bubbles from the micro-bubble system was below 0.42 μm ; their numerical density exceeded 2.9×10^4 counts/mL. With the same reaction temperature, micro-bubbles increased specific surface area and provided more reaction sites, which effectively strengthened the mass transfer efficiency and promoted the reaction of sodium persulfate and methylene blue.

4. Conclusion

The degradation rate of methylene blue reached to 91.3% at 90th min in the MAR, whereas reached to 85.7% at 250th min in the HTAR. In addition, the reaction rate constant in the MAR is 6.52 times than that in the HTAR. Based on the fitted models, it can be indicated that the reaction rate constant was 2.45 times in the micro-bubbles activated reactor than that in the high temperature activated reactor. Meanwhile, the special performance of the micro-bubbles provided more free radicals and reaction sites, which would effectively, strengthened the mass transfer efficiency and promoted the reaction of sodium persulfate and methylene blue.

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