REMOVAL OF DISPERSE RED 152 USING OZONE COMBINED WITH ULTRASOUND

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ABSTRACT

The removal of organic dyes from wastewater is essential to protect the ecosystem and human health. This study evaluated the ability of the ozone system combined with ultrasound to remove organic pigment disperse red 152 (DR152). Factors affecting DR152 removal efficiency such as the combined effects of ozone and ultrasound, pH of the solution, ozone dose, DR152 concentration, and temperature have been systematically studied. The results showed that the combination of ozone and ultrasound increased removal efficiency significantly with a combined coefficient of 1.72. The kinetics of the treatment process followed the first-order kinetic model. Optimal conditions for the treatment process included pH = 7, ozone dose of 700 mg/h, and temperature of 50 ^oC. The results also showed that the efficiency and reaction rate depended significantly on the initial concentration of the dye. The results obtained in this study demonstrate that the combined ozone and ultrasound system has great potential for application in removing organic dyes from wastewater.

NGHIÊN CỨU XỬ LÝ CHẤT MÀU DISPERSE RED 152 BẰNG PHƯƠNG PHÁP OZONE KẾT HỢP SIÊU ÂM

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TỪ KHÓA

Ozone
Sóng siêu âm
Kết hợp
Disperse Red 152
Hiệu suất loại bỏ

TÓM TẮT

Việc xử lý chất màu hữu cơ trong nước thải là rất cần thiết để bảo vệ hệ sinh thái và sức khoẻ của con người. Nghiên cứu này đã đánh giá khả năng xử lý chất màu dispersed red 152 (DR152) của hệ ozone kết hợp sóng siêu âm. Các yếu tố ảnh hưởng đến hiệu suất xử lý DR152 như ảnh hưởng cộng hợp của ozone và sóng siêu âm, pH của dung dịch, hàm lượng ozone, nồng độ chất màu và nhiệt độ đã được nghiên cứu một cách hệ thống. Kết quả cho thấy sự kết hợp của ozone và sóng siêu âm làm tăng hiệu quả xử lý lên đáng kể với hệ số cộng hợp đạt 1,72. Động học của quá trình xử lý tuân theo mô hình động học bậc nhất. Điều kiện tối ưu cho quá trình xử lý bao gồm pH = 7, hàm lượng ozone bằng 700 mg/h và nhiệt độ bằng 50 ^oC. Kết quả cũng cho thấy hiệu suất và tốc độ xử lý phụ thuộc đáng kể vào nồng độ ban đầu của chất màu. Kết quả thu được trong nghiên cứu này chứng tỏ rằng hệ kết hợp ozone và sóng siêu âm có nhiều tiềm năng ứng dụng trong xử lý chất màu hữu cơ trong nước thải.

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1. Introduction

Wastewater containing organic dyes can significantly impact the environment if not appropriately treated [1]. These dyes can contribute to water pollution, leading to a range of ecological issues. The presence of dyes in water can alter its color and harm aquatic life, including fish, invertebrates, algae, and other aquatic plants. The toxicity of dyes may stem from their chemical composition and the byproducts of their degradation. Additionally, the accumulation of toxic dyes in the food chain can affect higher trophic levels, including birds and mammals. Therefore, the treatment of wastewater containing organic dyes is imperative to minimize environmental impacts and safeguard water resources.

Ozone is recognized as a potent oxidizing agent capable of oxidizing a wide range of substances, including organic compounds, metals, and microorganisms. Due to its strong oxidative properties, ozone is employed in the treatment of wastewater containing organic pollutants. This application leverages the ability of ozone to degrade various organic pollutants into simpler, less harmful compounds [2]. The oxidation process with ozone involves breaking the chemical bonds within organic pollutants, resulting in the formation of simpler compounds that can be more easily removed [3]. A significant advantage of ozone treatment is its efficacy in decomposing numerous types of organic pollutants within a short timeframe [4]. Ultrasonication represents a widely adopted technique in wastewater treatment, attributed to its efficacy in removing a diverse array of pollutants, including organic and inorganic compounds, suspended solids, and pathogens [5]. Ultrasonic waves operate by generating high-frequency sound waves, typically above 20 kHz, which induce pressure oscillations in the water. These pressure waves lead to the formation and subsequent collapse of microbubbles filled with gas. The implosion of these bubbles generates localized intense energy, producing high temperatures, pressures, and shear forces, which contribute to the decomposition and elimination of pollutants [6].

The integration of ozone and ultrasonication technologies has been demonstrated to significantly enhance the efficiency of wastewater treatment processes through synergistic effects [7]. This combination is known to augment the production of hydroxyl radicals, which are highly effective in breaking down pollutants. The high energy generated by ultrasonication can also disrupt the cell walls of bacteria and other microorganisms, rendering them more susceptible to oxidation by ozone [8]. In the study conducted by Shen et al. [4], the effects of combining ozone with ultrasonication for the degradation of X-3B were investigated. The results indicated that the O-U system exhibited a higher treatment efficiency compared to the use of ozone or ultrasonication alone. The calculated synergy coefficient reached 1.42. Furthermore, in research [8], the treatment of wastewater from gold refining processes containing cyanide ions was explored using the combined ozone and ultrasonication approach. The authors reported that this integration could comprehensively treat wastewater containing cyanide, effectively destroying cyanide and facilitating additional copper recovery. The removal rate of cyanide and the copper recovery rate achieved were 99.96% and 99.3%, respectively, under optimal conditions of ozone flow rate at 80 L/h, temperature at 25 °C, reaction time of 15 minutes, and ultrasonic energy density of 80 W/L.

This study aims to evaluate the treatment process of disperse red 152 (DR152) utilizing a combination of ozone and ultrasonication. A systematic investigation was conducted on various factors influencing the treatment process, including the synergistic effects, pH, ozone concentration, dye concentration, and temperature.

2. Experiment

The treatment system for disperse red 152 (DR152) employing a combination of ozone and ultrasonication is depicted in Figure 1. The system comprises a reaction vessel made from polyethylene (PE), an ozone generator, and an ultrasonic bath. Initially, 1000 mL of the DR152 solution, with predetermined concentration and pH, was introduced into the reaction vessel. Subsequently, ozone gas was infused into the solution via a gas distribution system from the ozone generator, while ultrasound at a frequency of 40 kHz was applied to the treatment system. At specific time intervals, 2 mL of the solution was extracted for analysis. The concentration of DR152 in the solutions was determined on a V-770 (Jasco) spectrophotometer at a wavelength of 528 nm. The removal efficiency (%) was calculated using the following formula:

$$\text{Removal efficiency} = \frac{C_o - C_t}{C_o}\ 100\% \quad (1)$$

where C_o and C_t are the DR152 concentrations (mg/L) of the initial solution and the treated solution after t minutes, respectively.

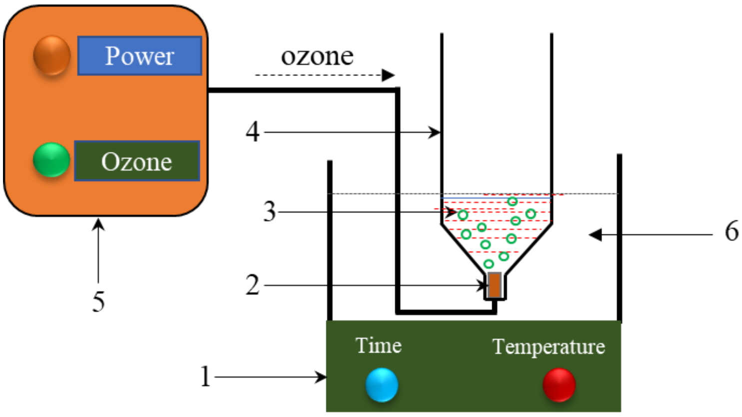


Figure 1. *Experimental diagram of treating DR152 with ozone combined with ultrasound: (1) - ultrasonic bath; (2)-ozone gas distribution disc; (3)-DR152 solution; (4)-Reaction vessel; (5)-ozone generator; (6)-water*

To study the synergistic effect of ultrasound and ozone, three series of experiments were performed with a DR152 concentration of 200 mg/L at pH = 6. In the first series of experiments, the solution was only affected by ultrasound, and in the second series only ozone was used with a capacity of 1000 mg/h. In the third series of experiments, the solution was simultaneously subjected to ultrasound and ozone. The influence of pH on the efficiency of DR152 treatment with the O-U system was studied by changing the pH value of the reaction solution from 2 to 10 and the concentration of the initial DR152 solution was 200 mg/L. To evaluate the effect of ozone dose on the treatment performance of the O-U system, the ozone content in the experiments was changed from 200 to 1000 mg/h. These experiments were all conducted at pH = 7, DR152 concentration of 200 mg/L, and treatment time of 10 minutes. The effect of DR152 concentration on treatment efficiency was determined by changing its concentration from 100 to 600 mg/L. To study the effect of temperature on DR152 treatment performance, experiments were conducted at different temperatures of 30, 40, 50, 60, and 70 ^{o}C.

3. Results and Discussion

3.1. The synergistic effect of ultrasound and ozone

To evaluate the synergistic effects of ultrasound and ozone in the treatment process, the experiments were conducted under conditions of ultrasound, ozone, and combined ozone-ultrasound. The outcomes are presented in Figure 2. The results indicate that the treatment efficiency for the sample subjected to ultrasound alone was significantly low, achieving only 8.74% after 14 minutes. For the sample treated with ozone alone, the efficiency was considerably higher, approximately 84% after 14 minutes of treatment. The highest treatment efficiency was observed when combining ultrasound and ozone, exceeding 99% after 14 minutes. The combination of ozone and ultrasound demonstrated synergistic effects that enhanced their individual capabilities [4]. Ultrasound promotes the formation of additional hydroxyl radicals, thereby enhancing the oxidative capacity of the ozone treatment process. The synergistic effect results in a higher concentration of potent oxidizing agents, thus accelerating the decomposition of DR152. Ultrasound increases mass transfer within the reaction system due to its ability to enhance the mixing of substances and improve the dispersion of ozone in the solution. This ensures better contact between ozone and the dye, increasing the overall effectiveness of ozone usage. The increased decomposition efficiency achieved through the synergistic effect allows for lower concentrations of ozone, reducing operational costs and minimizing the formation of potentially harmful byproducts.

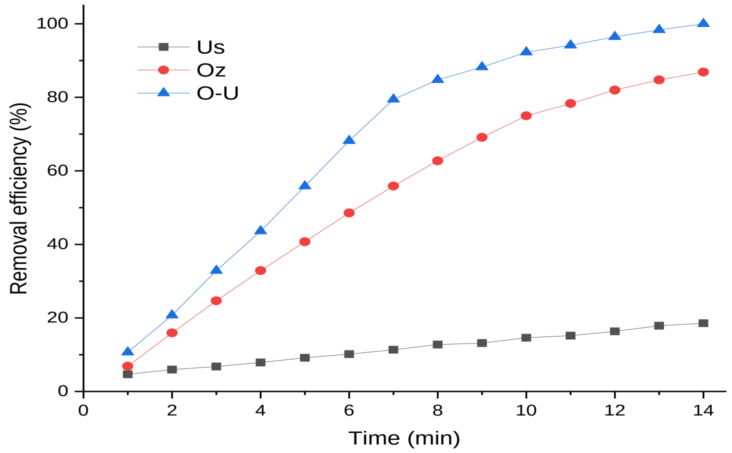


Figure 2. *Treatment efficiency of DR152 by different systems: ultrasound (Us, black), ozone (Oz, red), and ozone-ultrasound (O-U, blue) at pH value=6, temperature 30 °C, and dye concentration of 200 mg/l*

To evaluate the synergistic effect of ozone, the synergistic coefficient was calculated according to the formula [4]:

$$E = k_{U\text{-}O}/(k_{Oz} + k_{Us}) \quad (2)$$

where $k_{U\text{-}O}$, k_{Oz}, k_{Us} are the rate constants for the DR152 decomposition reaction in the ultrasound system (Us), ozone (Oz), and combined ozone with ultrasound (O-U), respectively. These constants were determined through analysis of experimental data using a first-order kinetic model which is mathematically presented as the following equation:

$$Ln(C_t/C_o) = -k*t \quad (3)$$

where C_o and C_t are the DR152 concentrations before and after the reaction time of t minutes, and k is the reaction rate constant. The calculation results from the first-order kinetic model for the three systems are given in Table 1.

Table 1. *Regression coefficients and rate constants calculated from first-order kinetic model*

System	Kinetic equation	Rate constant	R^2
Us	$Ln(C_t/C_0) = -0.016t$	0.016	0.981
Oz	$Ln(C_t/C_0) = -0.133t$	0.133	0.989
U-O	$Ln(C_t/C_0) = -0.257t$	0.257	0.969

The correlation coefficient R^2 for all three systems exceeds 0.95, indicating that the experimental data for each system align well with a first-order kinetic equation. There is a significant difference in the rate constants among the systems, with the ozone-ultrasound (O-U) system exhibiting the highest rate constant. The synergy coefficient E equals 1.72, demonstrating that the combination of ozone and ultrasound in the treatment system enhances the treatment rate. This synergy likely stems from the enhanced generation of reactive species and improved mass transfer, leading to more efficient degradation of contaminants.

3.2. Effect of pH on DR152 removal efficiency

In the process of treating organic substances using the O-U (ozone-ultrasound) method, the pH value of the reaction solution plays a critical role because it affects the state of existence of organic substances, the oxidizing potential of ozone, the ability to form free radicals, and the interaction between oxidants and organic materials. To investigate the impact of solution pH on the treatment efficiency of DR152, experiments were conducted across a range of pH values from 2 to 10. The results, presented in Figure 3, reveal a significant dependence of DR152 removal efficiency on the pH. The treatment efficiency increased as the pH value rose from 2 to 7. However, for samples at pH = 8, the removal efficiency at various time intervals was lower than that for samples at pH = 7. The influence of pH can be elucidated as follows: at low pH values, the concentration of hydroxyl ions (OH-) is relatively low. Consequently, the generation of free hydroxyl radicals is restricted, leading to a decrease in the removal efficiency; as the pH of the solution increases to 7, ozone becomes more stable at higher pH values, allowing it to persist in the solution for a longer duration. This enhances the availability of ozone for oxidation reactions, resulting in improved performance. However, when pH exceeds 7, the solubility of ozone in the solution decreases, leading to a reduced capability of ozone to participate in oxidation reactions. From the obtained results, it can be concluded that a pH of 7 is optimal for the treatment of DR152 using the combined ozone-ultrasound process.

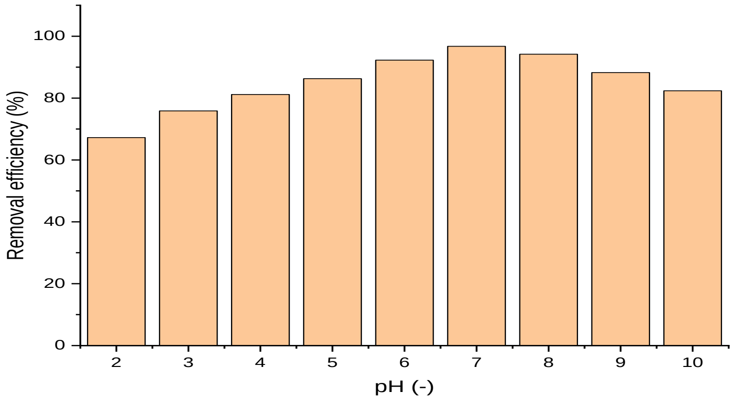


Figure 3. *Effect of pH on DR152 removal efficiency by O-U method*

3.3. Effect of ozone dose on DR152 removal efficiency

In the O-U method, the ozone dose is a critical parameter influencing the treatment efficiency. To assess the impact of ozone dose on treatment performance, experiments were conducted at a pH of 7, with a dye concentration of 200 mg/L and a treatment time of 10 minutes. The ozone dose in these experiments was varied across different levels including 200, 300, 400, 500, 600, 700, 800, 900, and 1000 mg/h. The relationship between the removal efficiency and ozone dose is depicted in Figure 4. The results demonstrate that the removal efficiency rapidly increases from 30.87% at 200 mg/h to 45.72%, 61.98%, 77.89%, 90.84%, and 96.73% for ozone concentrations of 300, 400, 500, 600, and 700 mg/h, respectively. However, when the ozone dose increases to 800, 900, and 1000 mg/h, the removal efficiency shows little change. The influence of ozone concentration on efficiency can be explained as follows: at lower ozone doses (200-600 mg/h), the removal efficiency of DR152 increases due to the higher ozone dose, which raises the concentration of ozone molecules in the solution, leading to stronger oxidation reactions with the organic dye; once the ozone dose reaches 700 mg/h, further increases do not improve dye removal efficiency due to ozone concentration saturation. From these results, it can be concluded that an ozone concentration of 700 mg/h is optimal for the treatment process of DR152 using the O-U system.

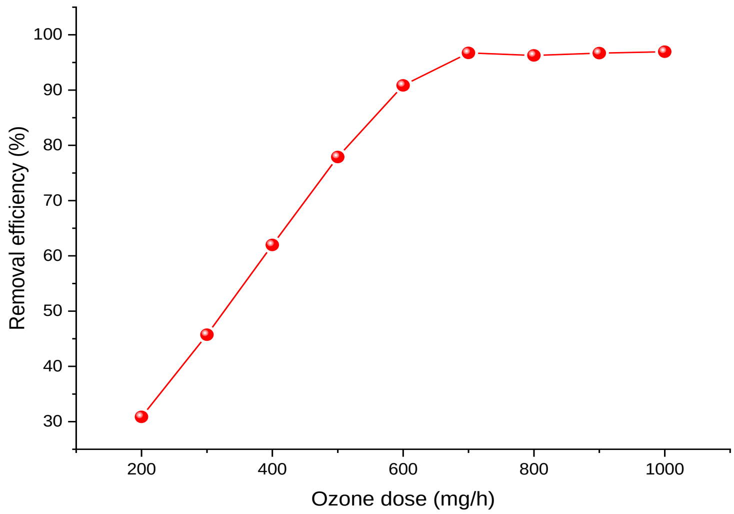
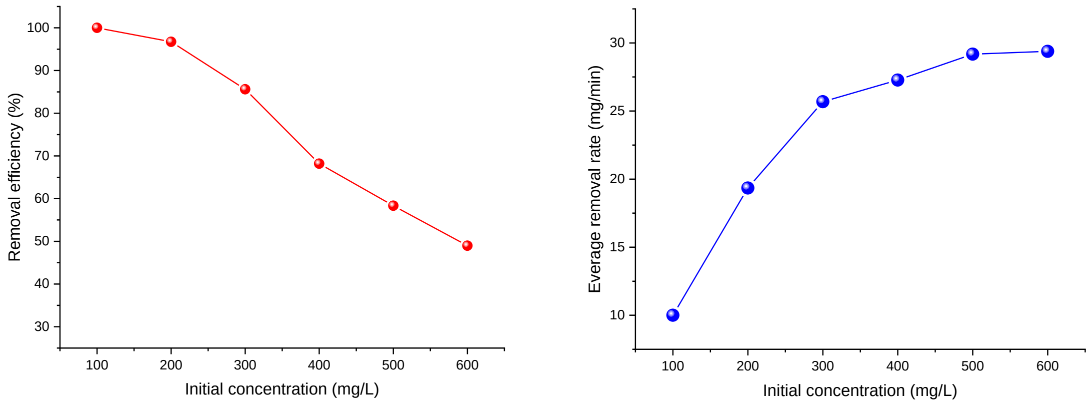


Figure 4. *Effect of ozone dose on DR152 removal efficiency*

3.4. Effect of DR152 initial concentration on the removal efficiency

In this study, the effect of the initial concentration on the removal efficiency was investigated through experiments with solutions of varying DR152 concentrations, ranging from 100 mg/L to 600 mg/L. Samples were analyzed for DR152 content after 10 minutes of treatment, and the results are presented in Figure 5(a). It is evident that the treatment efficiency of DR152 is heavily dependent on the initial concentration of the dye. For the sample at 100 mg/L, DR152 was completely degraded, whereas at 400 mg/L, the efficiency reached about 68%, at 500 mg/L, the efficiency was only 53%, and at 600 mg/L, it was 48%. This phenomenon can be attributed to factors related to reaction kinetics and mass transfer limitations. As the dye concentration increases, the ratio of ozone to dye decreases, and the amount of ozone is insufficient for the oxidation reactions of the dyes. Consequently, this reduces the efficiency of the treatment process.



(a) *(b)*

Figure 5. *Effect of DR152 initial concentration on the removal efficiency (a), and average degradation rate (b)*

To further evaluate the effect of the initial concentration of the removal rate, the DR152 average removal rate of the ozone-ultrasound system was calculated using the following equation:

$$\text{Everage removal rate} = (C_o - C_t) * V/t \quad (4)$$

where V is the solution volume and t is the reaction time. The results are given in Figure 5(b). It can be seen that the average degradation rate depends significantly on the initial DR152 concentration. When the concentration increases from 50 to 300 mg/L, the average removal rate increases rapidly and then slightly increases at the higher concentrations (400 and 500 mg/L). This can be explained that when the concentration of DR152 increases, the possibility of collision between DR152 and ozone increases, causing the average reaction rate to increase. However, when the DR152 concentration increases, the ozone/DR152 ratio decreases, so the average treatment rate increases slowly. From this result, it can be seen that for ozone-ultrasonic treatment of DR152, optimization between performance and processing rate is very important.

3.5. Effect of temperature on the removal efficiency

In the ozonation process, temperature is a key factor because it affects the rate of oxidation reaction of ozone on dyes and affects the solubility of ozone. In this study, to evaluate the effect of temperature on the DR152 treatment efficiency of the O-U system, experiments were performed at pH = 7, DR152 concentration of 300 mg/L for 10 minutes, and at temperatures of 30, 40, 50, 60, and 70 ^{o}C. The effect of reaction temperature on treatment efficiency is presented in Figure 7. The results show that treatment efficiency increases from 85% at 30 ^{o}C to 90% and 95% when the temperature increases to 40 and 50 ^{o}C. However, if the temperature continues to increase to 60 and 70 ^{o}C, the treatment efficiency drops to 93 and 78%, respectively. This trend can be explained by the combined effects of reaction kinetics, mass transfer, and chemical stability. Higher temperatures often enhance the reaction kinetics of chemical processes. The reaction between ozone and organic matter is typically faster at higher temperatures due to increased molecular collision rates and higher activation energies [9]. Therefore, the removal efficiency of ozone ultrasonic systems tends to increase with temperature. However, at higher temperatures, the solubility of ozone in water decreases. This reduced solubility reduces the availability of ozone molecules for oxidation and degradation of organic dyes. Therefore, removal efficiency may be adversely affected at high temperatures (above 50-60°C) due to reduced ozone mass transfer into solution. Additionally, intermediate products formed during oxidation can also exhibit different stability properties at different temperatures, potentially affecting the overall removal efficiency.

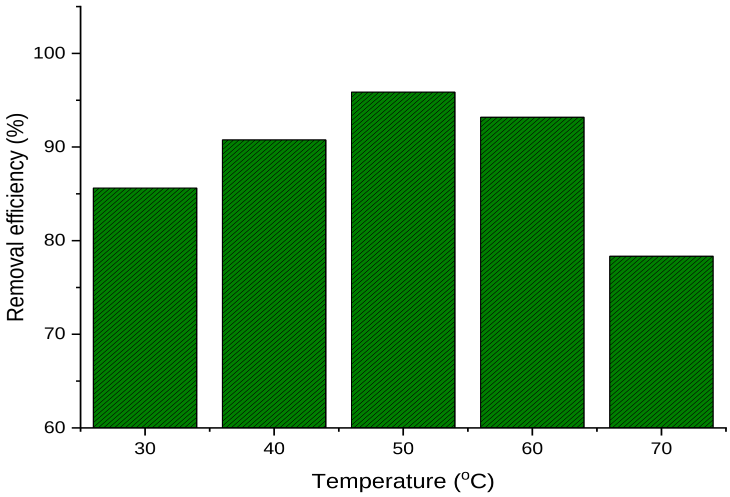


Figure 6. *Effect of temperature on DR152 removal efficiency using the O-U system*

4. Conclusion

The feasibility of the O-U system in removing DR152 from the aqueous solution has been evaluated. The combined effects of zone and ultrasound sound, pH of solution, ozone dose, DR152 concentration, and temperature on DR152 removal efficiency have been thoroughly investigated. It was found that the combination of ozone and ultrasound enhanced the removal efficiency remarkably and the calculated synergetic coefficient was 1.72. The first-order kinetic model could well predict the experimental data. Optimal conditions for the removal process were a pH of 7, an ozone dose of 700 mg/h, and a temperature of 50 ^oC. The removal efficiency was noticeably affected by the initial concentration of DR152. In the initial concentration range of 50-300 mg/L, the removal efficiency was above 80% while at the higher concentration (400 and 500 mg/L), the efficiency decreased significantly. The results obtained in this study show that the combination of ozone and ultrasound in a system demonstrates great potential for application in removing organic dyes from wastewater.

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