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Research Article

Oxidation Degradation of Rhodamine B in Aqueous by UV/$S_2O_8{}^{2-}$ Treatment System

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The UV photolysis of persulfate ($S_2O_8{}^{2-}$) is a novel advanced oxidation technologies (AOTs), which leads to the formation of strong oxidizing radicals, sulfate radicals ($SO_4{}^{\bullet -}$). The effect of oxidant $S_2O_8{}^{2-}$ concentration, initial dye concentration, initial pH of solution, and various inorganic anions (Cl^-, $H_2PO_4{}^-$, and $HCO_3{}^-$) were investigated using Rhodamine B (RhB), a kind of xanthene dye, as a model pollutant. With the increase of oxidant $S_2O_8{}^{2-}$, more $SO_4{}^{\bullet -}$ produced to attack RhB molecules and result in the increase of RhB degradation. While the improvement was not sustained above a critical value, beyond which degradation rate does not increase. Initial pH of solution had great effect on the RhB degradation rate during UV/$S_2O_8{}^{2-}$ system. $SO_4{}^{\bullet -}$ is rather stable in acidic solutions, while increasing system pH results in the transformation of $SO_4{}^{\bullet -}$ to ${}^{\bullet}OH$. The effects of three inorganic anions (Cl^-, $H_2PO_4{}^-$, and $HCO_3{}^-$) all had some negative effect on the degradation of RhB. Based on the RhB solution changes of the UV-vis absorption intensity during the UV/$S_2O_8{}^{2-}$ treatment, decolorization of RhB accompanied the destruction of aromatic ring structures of RhB molecules.

1. Introduction

Dyes are widely used in textile, leather, pharmaceutical, plastic, paint, and food industries [1].

Nearly more than 800,000 tons dye are produced per year, and over 15% of the synthetic textile dyes used are lost during manufacturing or processing operations and released as effluents [2, 3]. The effluents will produce adverse effects on the ecoenvironments due to their nonbiodegradability, toxicity, potential carcinogenic and mutagenic nature [3, 4]. For the treatment of dye-containing wastewater, traditional physicochemical techniques such as adsorption on activated carbon, membrane separation and coagulation have difficulties in the complete destruction of dye pollutants [5].

Advanced oxidation technologies (AOTs) are attractive alternatives to nondestructive physical water treatment processes because they are able to mineralize organic contaminants. AOTs, such as Fenton reagent, photo-Fenton, UV/O_3, UV/H_2O_2, and TiO_2-mediated photocatalysis processes based on the generation reactive hydroxyl radicals (${}^{\bullet}OH$), have emerged to be promising alternatives for dye-off wastewaters [6–9].

In recently, sulfate radicals-based AOTs have come forth for the degradation of nonbiodegradable compounds [10–14]. The rapid destruction of organic contaminants by sulfate radicals ($SO_4{}^{\bullet -}$) at a near diffusion-controlled rate ($10^9\ M^{-1}\cdot s^{-1}$) has gained great interest among practitioners as a potential method for on-site hazardous waste remediation [15]. Compared to ${}^{\bullet}OH$, $SO_4{}^{\bullet -}$ demonstrate higher reduction potential at neutral pH and are more selective for oxidizing organic pollutants [16]. In general, $SO_4{}^{\bullet -}$ can be generated by scission of peroxide bond by radiolytic, photolytic, and thermal activation of persulfate ($S_2O_8{}^{2-}$), or electron transfer by transition-metal activation of $S_2O_8{}^{2-}$ or peroxymonosulfate [17–20]. Among them, UV-mediated decomposition of persulfate (UV/$S_2O_8{}^{2-}$) is an efficient oxidative system that can form $SO_4{}^{\bullet -}$ as major oxidizing species. Similar to H_2O_2, $S_2O_8{}^{2-}$ shows significant photochemical activity under the UV irradiation. $S_2O_8{}^{2-}$ is the most important oxidant used as $SO_4{}^{\bullet -}$-based oxidants

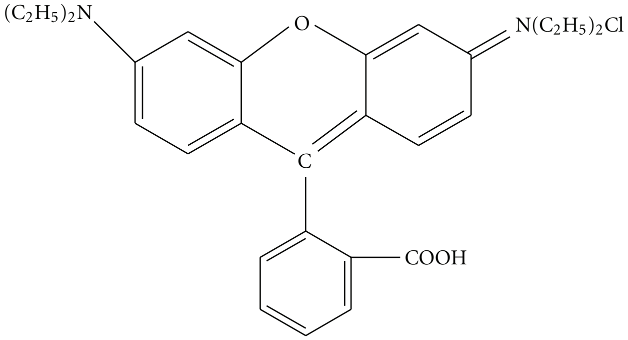

Figure 1: Structure of Rhodamine B.

and thus has drawn increasing attention as an alternative oxidant in the chemical oxidation of contaminants [11–15, 19–21]. The use of $S_2O_8{}^{2-}$ has several advantages. $S_2O_8{}^{2-}$ itself is a strong oxidant with a standard oxidation potential of 2.01 V comparable to O_3 (2.07 V), nonselectively reactive, and relatively stable at room temperature [10, 19–21]. Moreover, a low cost of $S_2O_8{}^{2-}$ facilitates $SO_4{}^{\bullet -}$-based AOTs for potential application in wastewater treatment.

In this work, a model refractory organic dye pollutant Rhodamine B (RhB), which contains four N-ethyl groups at either side of the xanthene ring, was chosen as the target pollutant to examine the degradation behavior of the $UV/S_2O_8{}^{2-}$ system. RhB is an important representative of xanthene dye, widely used as a colorant in textiles and food stuffs, and is also a well-known water tracer fluorescent, which has the property of carcinogenicity, reproductive and developmental toxicity, neurotoxicity, and chronic toxicity towards humans and animals [6, 22]. The objective of this work was to investigate the factors that influence the degradation rate of RhB in $UV/S_2O_8{}^{2-}$ treatment system such as oxidant doses, initial dye concentration, and the effects of anions (Cl^-, $H_2PO_4{}^-$, and $HCO_3{}^-$) that are ubiquitous coexistent in waters on the degradation of RhB with the $UV/S_2O_8{}^{2-}$ system.

2. Experimental

2.1. Chemicals. RhB (Figure 1) was purchased from Alfa Aesar, A Johnson Matthey Company. $K_2S_2O_8$ was purchased from Tianjing Guangfu Company, China. All other chemicals were analytical grade and used as received without further purification. For pH adjustment, 0.1 M sulfuric acid and 0.1 M sodium hydroxide were used, and all the experiments were conducted in an air-conditioned room at 25 ± 2°C. Milli-Q water was used throughout this study. Triplicate ($n = 3$) experiments were conducted under the identical condition.

2.2. Photoreactor and Light Source. The photodegradation experiments were performed in an XPA-7 merry-go-round photochemical reactor (Xujiang Electromechanical Plant, Nanjing, China) with quartz tubes containing the reaction solutions. A 300 W high-pressure mercury lamp used for the photodegradation experiment under UV-vis irradiation immersed inside water-cooled quartz well. The light source irradiance spectra (Figure 2) were measured with a monochromator (Acton, SP-300). The light intensity (200–420 nm) in the center of the reactive solutions was 4.10 mW/cm^2 for the mercury lamp.

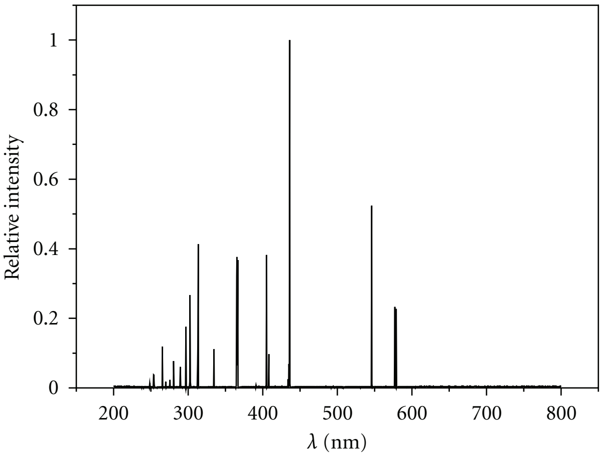

Figure 2: Irradiance spectra of the high-pressure mercury lamp light sources.

2.3. Experimental Procedure and Analysis. At specific intervals, samples were removed from exposure for UV-vis spectra measurement. The RhB degradation was characterized by measuring absorbency at 554 nm, the peak wavelength of RhB in the visible region. UV-vis spectra variations were recorded between 190 and 800 nm employing a Shimaduz 1700 UV-vis spectrometer.

3. Results and Discussion

3.1. Effect of Oxidants $K_2S_2O_8$ on the Photodegradation of RhB. The effect of oxidant $K_2S_2O_8$ on the degradation of RhB was investigated at natural pH, and the results were shown in Figure 3. Initially, control experiments were carried out in the absence and presence of either UV light or $K_2S_2O_8$ alone. Results showed that mere $K_2S_2O_8$ was not sufficient for the degradation of RhB. There was no observable color loss in the absence of UV irradiation. Only UV light irradiation, there was about 35% degradation of RhB with 60 min reaction time, while there was 85% with $UV/K_2S_2O_8$ ($[K_2S_2O_8] = 0.2$ mM) treatment system at the same reaction time, which is indicating that $UV/K_2S_2O_8$ was superior to UV alone in terms of the dye removal efficiency. The RhB degradation rate increased with the increasing of concentration of oxidant $K_2S_2O_8$ from 0.2 mM to 0.8 mM. While the improvement was not sustained above a critical value ($[K_2S_2O_8] = 1.0$ mM), beyond which the reaction rate decreased. This is mainly because that oxidant $K_2S_2O_8$ has two opposing effects [23, 24]. As the concentration of oxidant $K_2S_2O_8$ is increased, more $SO_4{}^{\bullet -}$ will be available to attack RhB molecules. Therefore, the rate of reaction increases. On the other hand, when $K_2S_2O_8$ is used in

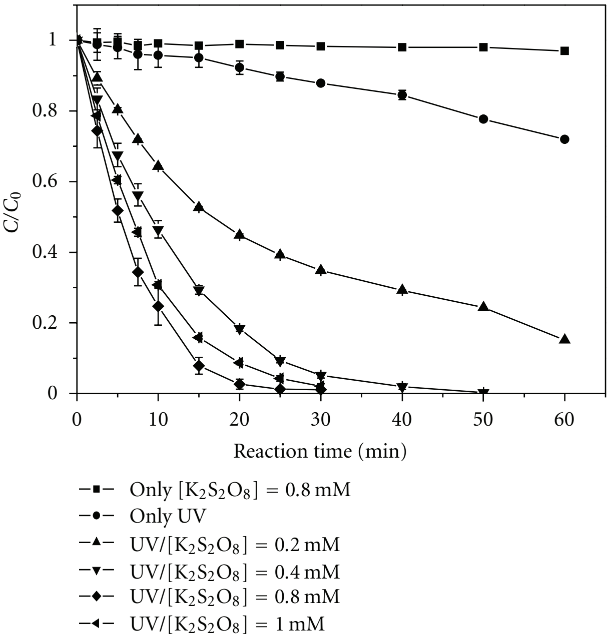

Figure 3: RhB degradation rate during UV/$K_2S_2O_8$ treatment system at different oxidant concentration. Conditions: [RhB] = 0.02 mM, no pH adjustment.

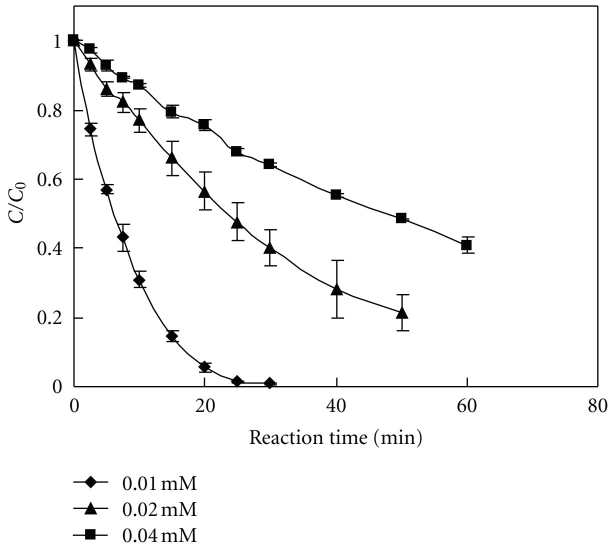

Figure 4: RhB degradation rate during the UV/$K_2S_2O_8$ treatment system at different dye initial concentration. Conditions: [$K_2S_2O_8$] = 0.4 mM, no pH adjustment.

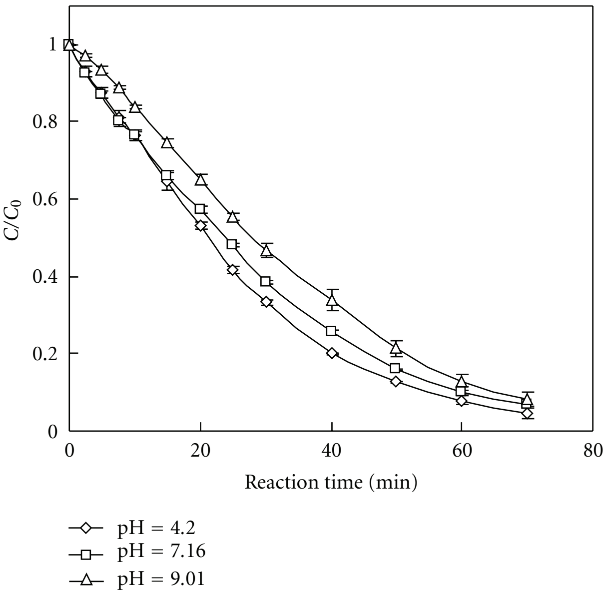

Figure 5: Effect of initial pH on the RhB degradation rate during the UV/$K_2S_2O_8$ treatment system. Conditions: [RhB] = 0.02 mM, [$K_2S_2O_8$] = 0.4 mM, no pH adjustment.

excess, $SO_4^{\bullet-}$ efficiently reacts with $K_2S_2O_8$ produce to $S_2O_8^{\bullet-}$, and $SO_4^{\bullet-}$ with $SO_4^{\bullet-}$ can dimerize to generate $S_2O_8^{2-}$.

3.2. Effect of the Initial RhB Concentration. The effect of dye initial concentration on the degradation efficiency was monitored, and the results were presented in Figure 4. It can be seen that photooxidation efficiency decreased as initial dye concentration is increased when the concentration of $K_2S_2O_8$ is constant. At high concentration of RhB, the penetration of photons entering into the solution decreases, so that an inner filter effect is induced, and hence the solution becomes more and more impermeable to UV radiation, consequently $SO_4^{\bullet-}$ concentration decreases. On the other hand, since the oxidant $K_2S_2O_8$ is constant and high concentration of RhB would consume more $SO_4^{\bullet-}$, the degradation rate would be decrease with the increase of the initial RhB concentration.

3.3. Effect of the Initial pH. To illustrate the effect of pH in the UV/$K_2S_2O_8$ treatment, the pH was adjusted to 4.20, 7.16, and 9.01, respectively. The results of pH dependency on the RhB degradation rate during UV/$K_2S_2O_8$ system at various initial pH were presented in Figure 5. When the initial pH was 4.21 and 9.01, the degradation efficiency was ~67.7% and 55.5% at 30 min, respectively. From the results, we can observe that acid initial pH has slightly positive effect on the RhB degradation during the UV/$K_2S_2O_8$ system. That is perhaps mainly because that $SO_4^{\bullet-}$ start to decompose and transform into $^{\bullet}OH$ rapidly with the pH increase [20, 25]. On the contrary, $SO_4^{\bullet-}$ are rather stable in acidic solutions. At low pH, the dominant active species is $SO_4^{\bullet-}$. In general, different pH values have not significant effect on the degradation of UV/$K_2S_2O_8$ system. Hence, the application of the combined UV/$K_2S_2O_8$ system will be of great significance because dye wastewater is usually in a broad range of pH.

3.4. Effect of Inorganic Ions. This study also examined the effect of anions on the decolorization of RhB such as Cl^-, $H_2PO_4^-$, and HCO_3^-, which are usually found in textile waste streams. The effect of three typical inorganic anion on the degradation of RhB with UV/$K_2S_2O_8$ was illustrated in Figure 6. It can be seen that all the anions used in this

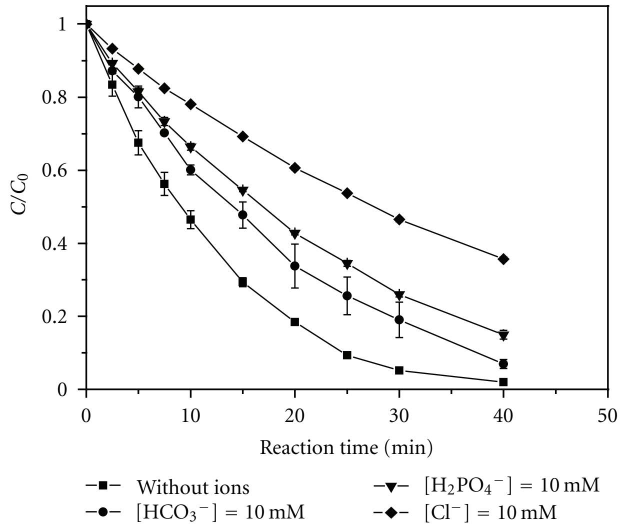

Figure 6: Influence of Cl^-, $H_2PO_4^-$ and HCO_3^- anions on the degradation of with UV/$K_2S_2O_8$ system. Conditions: [RhB] = 0.02 mM, [$K_2S_2O_8$] = 0.4 mM.

work inhibited the RhB degradation. It is well known that $SO_4^{\bullet -}$ can directly oxidize Cl^-, $H_2PO_4^-$, and HCO_3^- vis electron transfer reactions to produce less-active species [13, 26–28]. It is well known that $SO_4^{\bullet -}$ can directly oxidize Cl^-, $H_2PO_4^-$ and HCO_3^- vis electron transfer reactions to produce less-active species [13, 26–28]. The reaction rate constants for the reactions of $SO_4^{\bullet -}$ with HCO_3^-, $H_2PO_4^-$, and Cl^- are $\sim 10^6$ L/mol·s, $\sim 10^5$ L/mol·s and $\sim 10^8$ L/mol·s, respectively [28, 29]. The reaction rate constants of $SO_4^{\bullet -}$ with HCO_3^- and $H_2PO_4^-$ are less than that of Cl^- with $SO_4^{\bullet -}$. Hence, the inhibiting effect on RhB degradation of Cl^- is more obvious than HCO_3^- and $H_2PO_4^- \cdot SO_4^{\bullet -}$ were the dominant oxidative species in the UV/$K_2S_2O_8$ process, these anions were able to compete with RhB for $SO_4^{\bullet -}$ at various rate and thus led to the decrease of degradation of RhB.

3.5. The UV-Visible Absorption Spectra Analysis. In order to investigate the change in the molecule of RhB with the reaction time, UV-visible absorption spectra changes in the dye solution were observed, and the corresponding spectra are shown in Figure 7. It can be seen that there are two main characteristic absorption bands of RhB solution. One is UV region (259 nm), and another is in the visible region (554 nm). The UV band absorbance of dye solution at 554 nm ($n \rightarrow \pi$ transition of C=N, C=O groups) is due to the color of the dye solution, and it is used to monitor the decolorization of dye. Absorbance at 259 nm represents the aromatic content of RB, and the decrease of absorbance at this band indicates the degradation of aromatic part of dye [30]. During the UV/$K_2S_2O_8$ treatment system, absorption intensity of RhB in solution became weaker along with the reaction time. It can be explained that the aromatic ring structures of RhB molecules were destructed with reaction process.

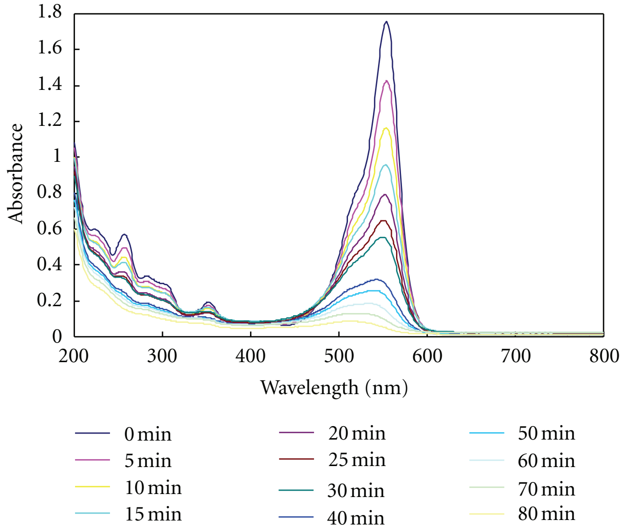

Figure 7: UV/Vis spectral changes of RhB with UV/$K_2S_2O_8$ treatment system. Conditions: [RhB] = 0.02 mmol/L, [$K_2S_2O_8$] = 0.4 mmol/L, no pH adjustment.

4. Conclusion

In this study, application of the UV/$K_2S_2O_8$ treatment processes to the aqueous degradation of RhB was investigated. The efficiency of the UV/$K_2S_2O_8$ system was investigated in terms of RhB decay. The effects of oxidants doses, initial RhB concentration anions, initial pH, and three kinds of anions (Cl^-, $H_2PO_4^-$ and HCO_3^-) on the degradation rate in the UV/$K_2S_2O_8$ system were investigated. The RhB degradation rate increased with the increasing of concentration of oxidant $K_2S_2O_8$ from 0.2 mM to 0.8 mM. While the improvement was not sustained above a critical value ([$K_2S_2O_8$] = 1.0 mM), photooxidation efficiency decreased as initial dye concentration increased at the same concentration of $K_2S_2O_8$. Acid initial pH facilitated the RhB degradation during the UV/$K_2S_2O_8$ system because that $SO_4^{\bullet -}$ are the dominant active species in this pH value area. In the UV/$K_2S_2O_8$ system, the observed adverse effects of inorganic anions could be the result of competitive with dye and the inhibiting effect followed the order of $Cl^- < H_2PO_4^- < HCO_3^-$. During the UV/$K_2S_2O_8$ treatment system, absorption intensity of RhB in solution became weaker along with the reaction time, which can be explained that the aromatic ring structures of RhB molecules were destructed with reaction process.

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