

Fe (III)-oxalate mediated solar degradation of reactive dyes in the presence of NaCl

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Abstract—NaCl was used for investigating its effect on the photocatalytic decomposition of two reactive dyes including Reactive Red 195 and Reactive Blue 222 in water using Fe (III)-oxalate complexes/H₂O₂ system under sunlight irradiation. Some important variables such as NaCl dosage and solar irradiation intensity were examined. Dye degradation and mineralization were examined and compared by UV-Vis spectrum and TOC measurements, respectively. The results indicate that dye decomposition was significantly reduced by the presence of NaCl on cloudy day. Moreover, increasing NaCl concentration could give rise to low degradation efficiency.

Keyword— Reactive dye; NaCl; degradation, solar light, Fe (III)-oxalate complexes

I. INTRODUCTION

More than 50% of cotton products are colored with reactive dyes, which are also the most unfavorable colorants from the ecological point of view. Inorganic salts are used as promoters in the coloration of cotton fabrics with reactive dyes [1]. Sodium chloride is the most commonly used inorganic salt in reactive dyeing of cotton fabrics. The addition of these Reactive Blue 222

inorganic salts in the dye bath increases the pollution load on the effluent generated as well as has an effect on various effluent treatment processes. Advanced oxidation processes (AOPs) can be considered as a promise alternative in decolorizing the textile dyeing effluents. Photo-Fenton process using Fe (III)-oxalate complexes is one of potential low cost AOPs, which can be run under solar irradiation because these species are photochemically active under sunlight [2]. In the past years, Fe (III)-oxalate complexes were used as catalysts in the photodegradation of textile dyes in water. The aim of this paper is to present results concerning the impacts of NaCl on the decomposition of reactive dyes using Fe (III)-oxalate complexes / H₂O₂ system under solar light. Some important variables such as NaCl concentration and intensity of solar irradiation (weather conditions) were examined with respect to decoloration percentage.

II. METHODS

Two reactive dyes used in this experiment included C. I. Reactive Red 195 and C. I. Reactive Blue 222, which were widely used in the dyeing of cellulose textiles in China. The chemical structures of both dyes were shown in Figure 1.

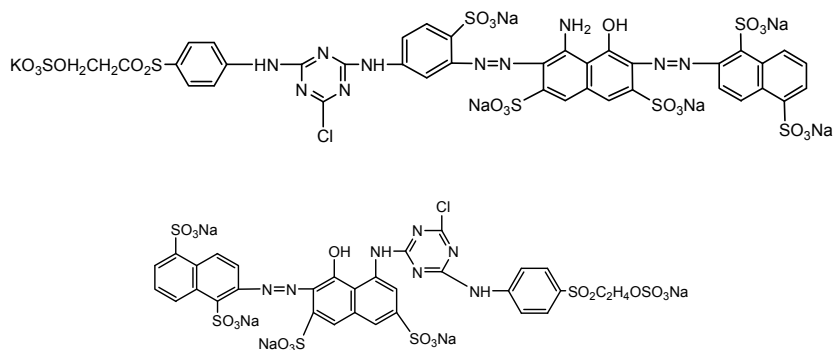


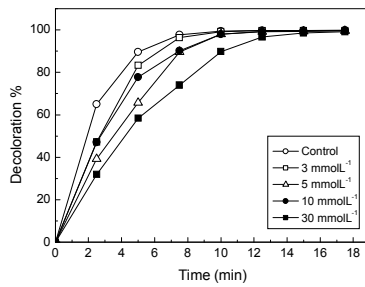
Figure 1. The chemical structures of both reactive dyes

Pyrex vessels of 150 ml capacity as reaction receivers held in a plastic rack at a 30° angle from the horizontal on the top of Chemical Engineering Building at the campus of Tianjin Polytechnic University about 9 m above sea level, 39.31° N, 117.98° E) on sunny or cloudy days at time from 10:00 to 14:30. The ambient temperature was 25-30 °C. The sunlight intensities were recorded using FZ-A radiometer that responds to light of 400-1000 nm and UV-A radiometer responding to the UV light of 365 nm, respectively. The reaction mixtures contain 0.045 mmolL⁻¹ dye, 0.20 mmol/LFe (III), 0.60 mmol/L oxalate ions, 1.0 mmol/L H₂O₂ and various concentration of NaCl at an initial of pH 3.5. Test solutions were then placed into reaction vessels and exposed to solar irradiation. At different time intervals, 1-2 ml of the sample was withdrawn

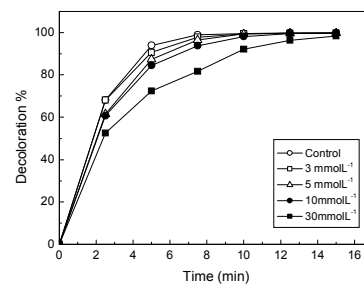
and diluted suitably, and the absorbance of which was measured at λ_{\max} of the dye solutions. The decoloration percentage of the dye was expressed as: $D\% = (1-C/C_0) \times 100\%$, where C_0 is the initial concentration of the dye and C is the residual concentration of the dye. Total Organic Carbon (TOC) was also measured and the TOC removal percentage of the dye was calculated as follows: $TOC\ removal\ \% = (1-TOC/TOC_0) \times 100\%$, where TOC_0 is the initial total organic carbon value of the dye solution and TOC is the residual total organic carbon value of the dye solution.

III. RESULTS AND DISCUSSION

A. NaCl concentration

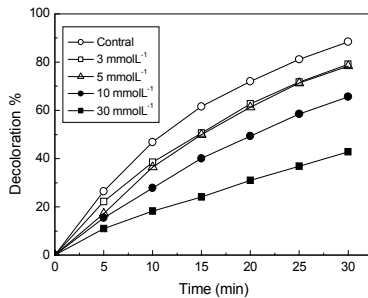


(a) Reactive Blue 222

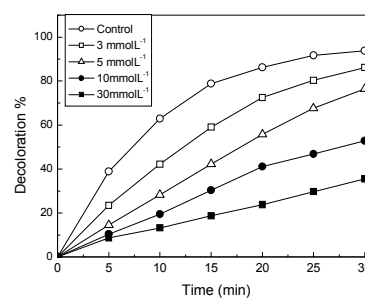


(b) Reactive Red 195

Figure 2 Effect of NaCl concentration on dye degradation on a sunny day: UV-A (365 nm): 0.677 (mW/cm²), Visible light (400-1000 nm): 22.5 (mW/cm²)



(a) Reactive Blue 222



(b) Reactive Red 195

Figure 3. Effect of NaCl concentration on dye degradation on a cloudy day, UV-A (365 nm): 0.191 (mW/cm²), Visible light (400-1000 nm): 5.51 (mW/cm²)

Figure 2 and Figure 3 show that $D\%$ values of the dyes gradually decreased with the increasing NaCl concentration in aqueous solution within exposure time, especially on a cloudy day. $D\%$ values on a sunny day were always higher than that

on a cloudy day at the same concentration of NaCl within the same exposure time. This may be owing to the hydroxyl radical scavenging effect of chloride ion. It has been confirmed that chlorine ion reacts with hydroxyl radical at

acidic pH, which in turn is converted to chlorine radical. Azo dyes react with chlorine radicals at much lower rate than with hydroxyl radicals. Hence, chlorine radicals significantly retard the dye oxidation [3, 4].

Another possible explanation is that adding NaCl is believed to increase the degree of aggregation of ionic dyes in water, which is sometimes called the “common ion effect” [1]. It has been concluded that enhanced aggregation can reduce solubility and ionization of the dyes in water and lower capability of dye molecules react with hydroxyl radicals. Comparing Figure 4 (a) and Figure 5(a), in the presence of

NaCl (30 mmol/L), Reactive Blue 222 was almost decolorized completely within 20 minutes in the clear sky. By contrast, just less than 50% $D\%$ values of Reactive Blue 222 were obtained at the same time under the cloudy sky. This indicates that the decoloration of the dyes was mainly determined by irradiation intensity and NaCl concentration. Moreover, higher solar irradiation could balance off the inhibition of NaCl on decoloration of the dyes because increasing irradiation intensity can accelerate photo-Fenton reaction, and generating more additional hydroxyl radicals, causing the high $D\%$ value.

B. UV-Vis spectrum

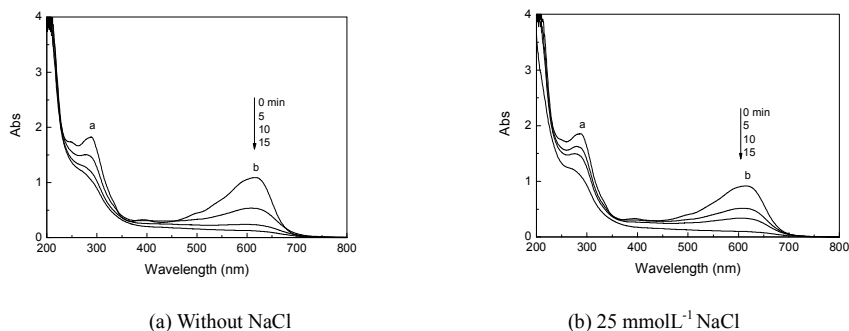


Figure 4. Changes in UV-Vis spectrum of Reactive Blue 222 on a sunny day: UV-A (365 nm), 0.714 (mWcm⁻²); Visible light (400-1000 nm), 26.5 (mWcm⁻²)

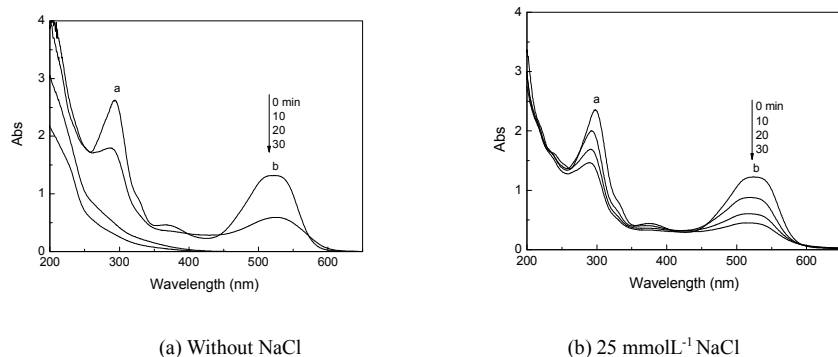
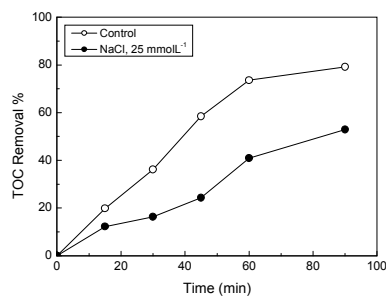


Figure 5. Changes in UV-Vis spectrum of Reactive Red 195 on a cloudy day: UV-A (365 nm), 0.180 (mWcm⁻²); Visible light (400-1000 nm), 5.89 (mWcm⁻²)

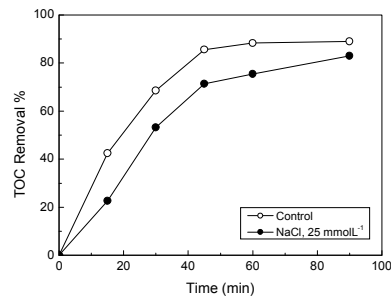
It is found from Figure 4 that addition of NaCl caused the slight changes in absorbance levels at 289 nm (Peak *b*) and 616 nm (Peak *a*) at the same exposure time compared with control experiment (without NaCl). On the other hand, it is noted that in Figure 5, the absorbance levels at 278.5 nm (Peak *b*) and 522 nm (Peak *a*) in the presence of NaCl are

much higher than those in the control experiment at the same exposure time on a cloudy day, suggesting that the salt reduced significantly not only decoloration, but also degradation (damage of aromatic parts) of the dyes under bad weather conditions.

C. TOC analysis



(a) Cloudy day



(b) Sunny day

Figure 6. Influence of NaCl on TOC removal % of Reactive Blue 222 on a cloudy day: UV-A (365 nm), 0.534 (mW/cm²); Visible light (400-1000 nm), 15.51 (mW/cm²) or on a sunny day: UV-A (365 nm), 0.714 (mW/cm²); Visible light (400-1000 nm), 26.5 (mW/cm²)

Figure 6 demonstrate that TOC removal % values of Reactive Blue 222 in the presence of NaCl are much less than those in control experiment (without NaCl) at the same condition, especially during the cloudy day. This indicates that the photocatalytic mineralization of the dye is more strongly effected by NaCl during the cloudy day than during the sunny day, which is well consistent with the decoloration and degradation reduced by NaCl above mentioned.

IV. CONCLUSIONS

Decomposition of two reactive dyes in water by photocatalysis of Fe (III)-oxalate complexes/H₂O₂ was undertaken in the presence of NaCl under different solar irradiation. It is summarized that high concentration of NaCl could enhance significantly retardant effect on the dye decomposition. Moreover, NaCl could limit more dramatically all the stages of decomposition including decoloration, degradation and mineralization of reactive dyes during sunny day than during cloudy day. The effect of NaCl on decomposition of reactive dyes is usually dependent on intensity of solar irradiation.

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