Removal of C.I. Reactive Red 2 by low pressure UV/chlorine advanced oxidation

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ABSTRACT

Azo dyes are commonly found as pollutants in wastewater from the textile industry, and can cause environmental problems because of their color and toxicity. The removal of a typical azo dye named C.I. Reactive Red 2 (RR2) during low pressure ultraviolet (UV)/chlorine oxidation was investigated in this study. UV irradiation at 254 nm and addition of free chlorine provided much higher removal rates of RR2 and color than UV irradiation or chlorination alone. Increasing the free chlorine dose enhanced the removal efficiency of RR2 and color by UV/chlorine oxidation. Experiments performed with nitrobenzene (NB) or benzoic acid (BA) as scavengers showed that radicals (especially $^{\cdot}$OH) formed during UV/chlorine oxidation are important in the RR2 removal. Addition of HCO_3^- and Cl^- to the RR2 solution did not inhibit the removal of RR2 during UV/chlorine oxidation.
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Introduction

Textile wastewater is an important contributor to environmental pollution of water in many countries. In China in 2012, textile industry discharges into waterways accounted for 11% and 9% of the total wastewater volumes and chemical oxygen demand discharges from all industrial sources, respectively (China Statistical Yearbook on Environment, 2013). Wastewater from dyeing and finishing processes plays a dominant role in pollution from the textile industry, because of the high concentrations of COD, salinity, colors, and toxic substances in these waste streams (Solís et al., 2012). Therefore, control of wastewater pollution from these sources has received increasing attention around the world.

Azo dyes are widely used in dyeing and finishing processes, and are present in 60%–70% of all commercial dyes (Işık and Sponza, 2005). Azo dyes are strong colorants, and have high bio-recalcitrance and toxicity because of their nitrogen–nitrogen double bonds (Cai et al., 2015). Untreated azo dye effluents are toxic and mutagenic to aquatic organisms in receiving waters (Panda and Mathews, 2014). Therefore, treatment technologies for removal of azo dyes are important.

Because azo dyes are bio-recalcitrant (Brown and Hamburger, 1987), chemical oxidation processes are frequently used to

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remove color from secondary effluents. Ozonation and Fenton oxidation are useful for removing some dyes. Ozonation quickly decolorizes colored wastewater *via* oxidative cleavage of the conjugated bonds in dye molecules (Tehrani-Bagha et al., 2010). Idel-aouad et al. (2011) found that the heterogeneous Fenton process using Fe(II)-exchanged synthetic Y Zeolite provided good performance in decolorization of a C.I. Acid Red 14 solution at pH 3.13–7.27. However, ozonation is very expensive, and Fenton oxidation produces large quantities of iron-containing sludge. Recently, the ultraviolet (UV)/H_2O_2 process has been considered as a promising technology for azo dye removal. UV/H_2O_2-generated hydroxyl radicals can react non-selectively with a broad range of organic compounds (Narayanasamy and Murugesan, 2014; Kasiri and Khataee, 2012). The principal advantage of the UV/H_2O_2 technology is that no sludge is created after treatment (Behnajady et al., 2006). However, H_2O_2 is expensive.

Recently, UV/chlorine oxidation has been reported as a novel advanced oxidation process (Feng et al., 2007, 2010). During UV/chlorine oxidation, free chlorine, including HOCl and OCl^-, absorbs UV photons and produces several radicals, including hydroxyl ($\cdot$OH) and chlorine ($\cdot$Cl) radicals (Nowell and Hoigné, 1992). The molar absorption coefficients of HOCl and OCl^- at 254 nm have been determined to be 59 ± 1 and 66 ± 1 L/(mol · cm) respectively (Feng et al., 2007), whereas the molar absorption coefficient of H_2O_2 at 254 nm is only 18.4 L/(mol · cm) (Stefan et al., 1996). During UV irradiation, HOCl has a much smaller $\cdot$OH scavenging rate than H_2O_2 (Watts and Linden, 2007). The yield of $\cdot$OH during the UV/chlorine oxidation process is affected by the oxidation conditions, including pH and concentrations of the pollutants. The $\cdot$OH radicals produced have been used for removing pollutants such as nitrobenzene, trichloroethylene, and iopamidol (Watts and Linden, 2007; Wang et al., 2012; Sichel et al., 2011). Furthermore,$\cdot$Cl radicals formed during the UV/chlorine oxidation process may also play an important role in pollutant degradation. In one study (Fang et al., 2014), the $\cdot$Cl radicals removed 62%–65% of the benzoic acid. Reaction rates of $\cdot$Cl with some compounds containing electrophilic functional groups, such as acetic acid, benzoic acid, and phenol, are much higher than those of $\cdot$OH (Fang et al., 2014). However, the removal of azo dyes using UV/chlorine oxidation, and especially under high salinity and alkalinity conditions, has not been reported.

The objective of this study was to evaluate the removal efficiency of azo dyes by low pressure UV/chlorine oxidation. The effects of UV irradiation doses, chlorine doses, pH values, and ion concentrations on azo dye removal during UV/chlorine oxidation were investigated. The roles of radicals during the UV/chlorine oxidation were also evaluated.

1. Materials and methods

1.1. Chemicals and materials

The commercial azo dye C.I. Reactive Red 2 (RR2) (CAS No. 17804-49-8) was obtained from Jiaying Chemical Company (Jiaying Chemical Company, Shanghai, China) and used without further purification. Sodium hypochlorite solution (13% available chlorine) was purchased from J&K Company (J&K, Beijing, China). Acetonitrile was of HPLC grade. Na_2SO_3 was of analytical grade. All solutions were prepared with ultrapure water (18.25 MΩ) from a Milli-Q purification system (Milli-Q, Millipore, USA).

1.2. RR2 degradation by UV/chlorine oxidation

The UV/chlorine oxidation experiments were conducted in a UV-C irradiation system with an 80-W UV-C lamp at 254 nm (80 W, Light Sources, USA) at 298 K. Free chlorine was added to RR2 solutions (20 mg/L initial RR2, 100 mL) in 120-mL beakers with an inner diameter of 10 cm to give free chlorine doses of 0–20 mg/L. Then the mixture was placed under the UV light and continuously stirred using magnetic agitators at ambient temperature (25 ± 2°C); a schematic diagram is shown in Fig. 1. The quantum yield was calculated at 0.740 ± 0.021 and the incident photon flux (I_0) was determined to be 0.325 μEinstein/sec using KI/KIO_3 actinometry (Bolton et al., 2011). The corresponding average UV fluence rate (E_{avg}) was about 2.0 mW/cm^2. The UV fluence was calculated as the fluence rate multiplied by the exposure time (Rosenfeldt et al., 2006). After UV/chlorine oxidation, Na_2SO_3 was used to remove residual chlorine in the solutions for subsequent RR2, color, and total organic carbon (TOC) analysis. All the experiments were conducted with at least duplicate measurements.

Experiments were conducted to evaluate the effect of pH on RR2 removal. The pH value of the dye solution was kept at 4, 7, 7.5, 8 or 9 by addition of phosphate buffer (final concentration 20 mmol/L).

To evaluate the effect of radicals on RR2 removal, NB and BA at final doses of 10 mg/L and 50 mg/L, respectively, were added into a RR2 solution containing free chlorine (5 mg free chlorine/L). NB was used to quench $\cdot$OH during UV/chlorine oxidation, while BA was a scavenger of $\cdot$OH and $\cdot$Cl.

1.3. Analytical methods

The RR2 concentrations in the solutions after UV/chlorine oxidation were determined by high performance liquid chromatography (LC20, Shimadzu, Japan) with detection at 538 nm. A reversed-phase column (ODS-C18, Bonna-Agela China, Tianjin, China) was used for separation, with a mobile phase of 50% acetonitrile and 50% ultrapure water at a flow rate of 0.5 mL/min.

The color, UV absorbance spectrum, and TOC values of the dye solutions after UV/chlorine oxidation were determined using a color analyzer (SD-9012, Xin Rui, China), ultraviolet–visible (UV–Vis) spectrophotometer (UV-2450, Shimadzu, Japan), and TOC analyzer (TOC-L, Shimadzu, Japan).

2. Results and discussion

2.1. Degradation of azo dye during UV/chlorine oxidation

2.1.1. Removal of azo dye and its color
The changes in dye concentration and color of RR2 solutions after UV/chlorine oxidation, after only UV irradiation, and after only chlorination are shown in Fig. 2. After only UV
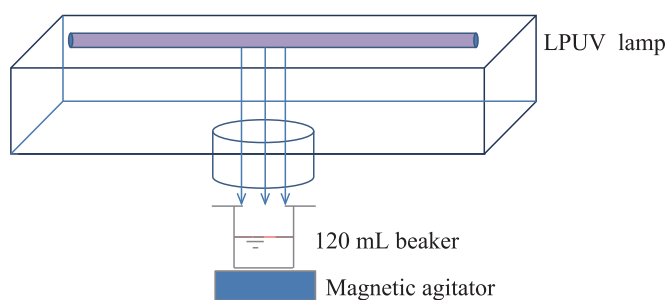
Fig. 1 – Schematic diagram of the UV irradiation system. LPUV: low pressure ultraviolet.

irradiation, the RR2 concentration and color did not change significantly, indicating that UV irradiation alone did not remove RR2 or its color. This result was supported by previous findings that showed there was no observable decrease in the dye concentration after UV irradiation of a dye solution (Muruganandham and Swaminathan, 2004; Mitrović et al., 2012).

After chlorination without UV irradiation, the RR2 concentration was 50.2% lower than before chlorination. The removal efficiency of RR2 increased from 26.9% to 50.2% when the chlorination time was increased from 1 to 10 min, while the color removal increased from 15.1% to 40.2% over the same period. It has been demonstrated that HOCl and OCl^- partly transform azo dyes into intermediates such as 1-chloro-4-nitrobenzene and 2-((4-chlorophenyl)(ethyl)amino)-ethanol (Vacchi et al., 2013).

It is interesting to note that after UV/chlorine oxidation, both the residual RR2 concentrations and color levels in the dye solutions were significantly lower than those before oxidation and after chlorination without UV. This indicates that combination of UV and free chlorine results in much stronger oxidation than UV or chlorination alone. The color removal efficiency was slightly lower than the RR2 removal

efficiency. This might be attributed to the generation of some colored intermediates during the UV/chlorine oxidation process.

Direct photolysis of $HOCl/OCl^-$ produces $^{\cdot}OH$ and $^{\cdot}Cl$, which can oxidize organic compounds into smaller molecules (Watts and Linden, 2007). The oxidation capacities of $^{\cdot}OH$ and $^{\cdot}Cl$ are much higher than that of free chlorine, with standard electrode potentials of $^{\cdot}OH$ and $^{\cdot}Cl$ at +2.7 and +2.4 V, respectively, compared with a free chlorine electrode potential of only +1.395 V (Buxton et al., 1988; Beitz et al., 1998; Snoeyink and Jenkins, 1980).

2.1.2. Changes in the spectrum and TOC
The UV–Vis spectral changes after UV/chlorine oxidation are shown in Fig. 3. Before treatment, the UV–Vis spectrum of RR2 showed five absorption bands, including a band at 538 nm, which is associated with azo bonds in RR2 (Wang et al., 2015). After UV/chlorine oxidation, the intensity of the bands in the UV–Vis spectrum of the RR2 solution decreased. For example, the absorbance at 538 nm decreased to 5.8% of the original value, which indicates that UV/chlorine oxidation decomposed the azo bond. The azo bond plays a key role in the color of RR2. Therefore, the reduction of absorbance at 538 nm supports the
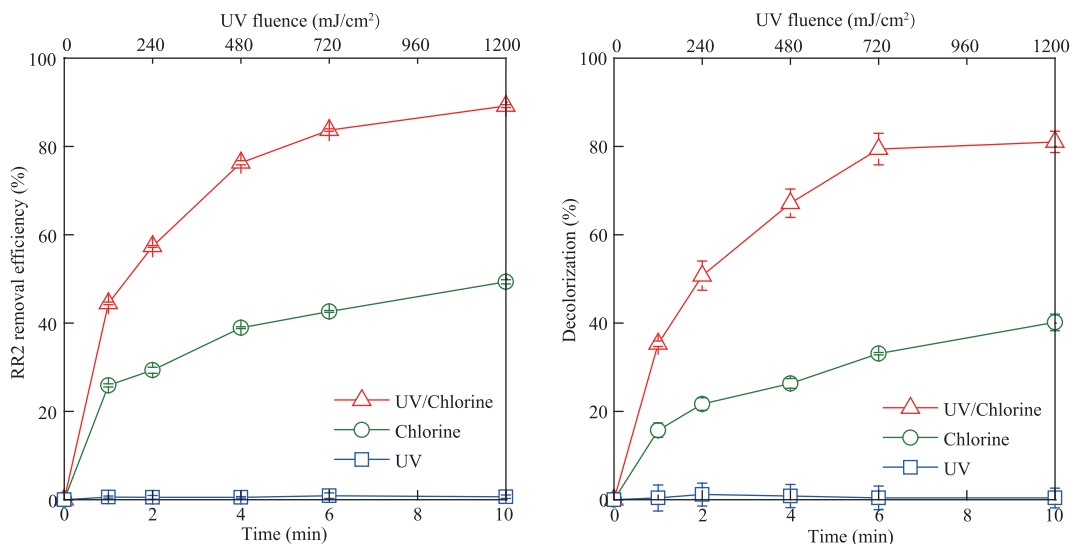

Fig. 2 – C.I. Reactive Red 2 (RR2) concentrations and color removal efficiencies during ultraviolet (UV)/chlorine oxidation at pH 7. Initial concentration of RR2 20 mg/L, UV fluence rate 2.0 mW/cm², and free chlorine dose 5 mg/L.

finding of increased color removal during UV/chlorine oxidation in this study.

The absorbance decrease in the UV–Vis spectrum of RR2 after UV/chlorine oxidation was similar to those in previous findings on ozonation and UV irradiation combined with Fenton oxidation, where after RR2 ozonation, the absorbance band at 538 nm and other bands also disappeared (Wu and Ng, 2008). The absorbance of the band at 538 nm also decreased after photocatalytic reaction in a $UV/H_2O_2/Fe^{2+}$ system (Wu et al., 2012).

With UV/chlorine oxidation, the TOC removal efficiency was very limited (data not shown), suggesting that UV/ chlorine oxidation did not convert RR2 into CO_2. Limited mineralization of azo dyes by the UV irradiation/H_2O_2 process was also reported in an earlier study, where only about 10% of TOC was removed after 55 min of UV irradiation of a C.I. Acid Orange 7 solution (Aleboyeh et al., 2008).

2.2. Effects of radicals on azo dye degradation

The changes in RR2 concentrations in the dye solutions after UV/chlorine oxidation in the presence of different concentrations of BA and NB are shown in Fig. 4. BA was used to quench both ·OH and ·Cl, while NB was a scavenger of ·OH. The reaction rate between NB and ·Cl is negligible (Watts and Linden, 2007).

In the presence of NB, the RR2 removal efficiency in the dye solution decreased with the increasing NB dose, which suggests that ·OH is important for enhancing RR2 removal by UV/chlorine oxidation. In the presence of BA, the RR2 removal efficiency also decreased greatly with the increasing BA dose, which indicates that ·OH and/or ·Cl are/is important in dye degradation.
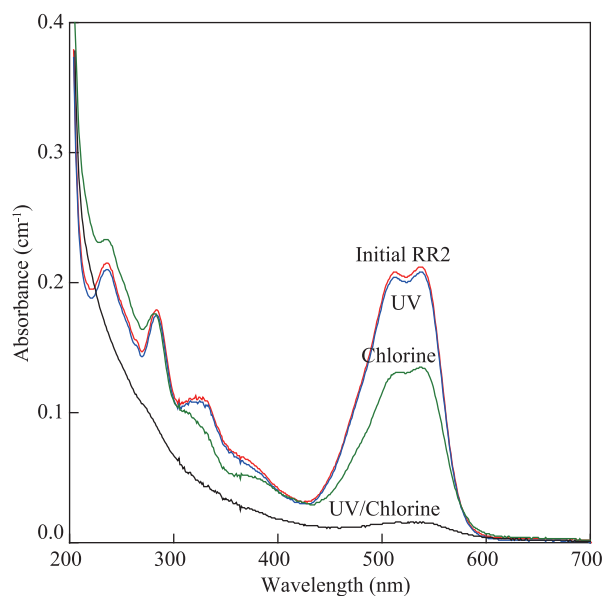

Fig. 3 – Changes in the UV–Vis absorbance spectrum in the RR2 dye solution during UV/chlorine oxidation at pH 7. Initial concentration of RR2 20 mg/L, UV fluence rate 2.0 mW/cm², irradiation time 10 min, and free chlorine dose 5 mg/L. UV–Vis: ultraviolet; RR2: C.I. Reactive Red 2; UV: ultraviolet.

It is interesting to note that the degradation efficiency of RR2 in the presence of BA was higher than that in the presence of NB at irradiation times of less than 6 min and scavenger concentrations of 10 mg/L (BA) and 50 mg/L (NB). However, this trend reversed with irradiation times of 10 min: RR2 removal efficiency in the presence of BA was slightly lower than that with NB addition. This indicates that radicals (especially ·OH) were important in the enhancement of azo dye degradation, and that the two radicals acted on the system in a different order. ·OH reacts with BA with a rate constant of 5.9×10^9 L/(mol · sec) and ·Cl reacts with BA with a higher rate constant of 1.8×10^{10} L/(mol · sec) (Buxton et al., 1988; Mártire et al., 2001). The rate constant of ·OH with NB was obtained as 3.9×10^9 L/(mol · sec) and the rate constant of ·Cl with NB was negligible (Buxton et al., 1988; Watts and Linden, 2007). It can be assumed that ·Cl reacts first with BA and then turns to ·OH in the presence of BA. Since addition of NaCl had little effect on the RR2 removal efficiency (see Section 2.3.3), Cl plays a minor role in the UV/chlorine oxidation (Kläning and Wolff, 1985). As a result, the removal efficiency in the presence of BA was higher than that in the presence of NB at irradiation times of less than 6 min. The roles of radicals during advanced oxidation processes using UV irradiation are very complex. In the UV/diketone process, the effect of ·OH on degradation of dyes was limited (Liu et al., 2014). However, Shu et al. (2014) found that in UV/chlorine oxidation, OH was the dominant contributor to the degradation of naphthenic acid in water polluted by oil sands, while ·Cl had a minor role. By contrast, Fang et al. (2014) found that ·Cl was important during UV/chlorine oxidation of benzoic acid. The differences between the results of the present study and those of earlier studies concerning the effects of ·OH and ·Cl suggest that the relative contributions of ·OH and ·Cl on pollutant removal are dependent on the specific pollutant.

2.3. Effects of process parameters and water quality on azo dye degradation by UV/chlorine oxidation

2.3.1. Effect of chlorine dose
Changes in the RR2 concentrations and color in the azo dye solutions after UV/chlorine oxidation for 6 min with different free chlorine doses are shown in Fig. 5. In the absence of UV irradiation, increasing the free chlorine dose from 0 to 10 mg of free chlorine per liter increased the degradation efficiency. However, when the free chlorine dose was increased to more than 10 mg of free chlorine per liter, further enhancement of RR2 degradation was very limited.

With UV irradiation, increasing the free chlorine dose greatly accelerated RR2 degradation. At a free chlorine dose of 7.5 mg of free chlorine per liter, the RR2 removal efficiency after UV/chlorine oxidation was about 97.9%, which was much higher than that after chlorination only. The results were similar for color removal after UV/chlorine oxidation and chlorination only. In UV/chlorine oxidation, HOCl/OCl⁻ are precursors of radicals, including ·OH and ·Cl. Increasing the free chlorine dose increased ·OH and ·Cl formation, and this enhanced removal of RR2 and color. An earlier study found that free chlorine as OCl⁻ was a key component for Methylene Blue photobleaching, and higher concentrations of OCl⁻
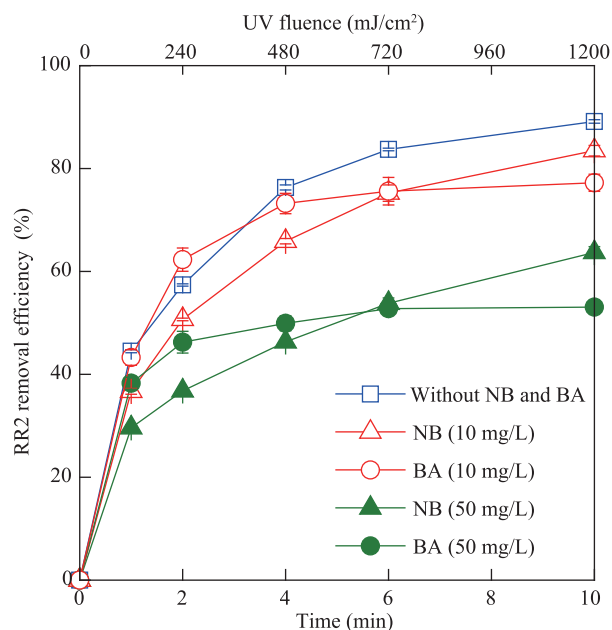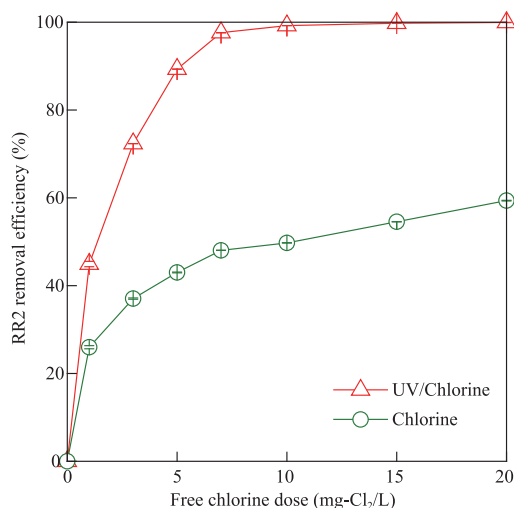
Fig. 4 – RR2 removal efficiency during UV/chlorine oxidation of RR2 solutions with and without addition of nitrobenzene (NB) and benzoic acid (BA) as radical scavengers. Initial concentration of RR2 20 mg/L, free chlorine dose 5 mg/L, pH 7, concentration of phosphate buffer 20 mmol/L, and UV fluence rate 2.0 mW/cm². RR2: C.I. Reactive Red 2; UV: ultraviolet.

generated more photoactive components for the Methylene Blue photobleaching reaction (Chan et al., 2012).

2.3.2. Effect of pH
The RR2 concentrations and color removal by UV/chlorine oxidation with different initial pH values are shown in Fig. 6.

The RR2 removal efficiencies by UV/chlorine oxidation at pH values between 7 and 8 were similar. However, under acidic and alkaline conditions (pH = 4 and 9), UV/chlorine oxidation exhibited limited RR2 removal efficiency. This indicates that the presence of H^+ or OH^- could reduce the capability of the radicals to remove RR2.

In this study, the absorbance at 254 nm of RR2 was constant at pH values from 4 to 9 (data not shown). The influence of pH on the dissociation of chlorine may explain the effect of pH on the removal efficiency of RR2. The dissociation of $HOCl/OCl^-$ ($pK_a = 7.5$) is sensitive to solution pH. At lower pH, HOCl dominates in the speciation of free chlorine; at higher pH, OCl^- is the predominant species (Feng et al., 2007). The quantum yields of HOCl and OCl^- photolysis at 254 nm at ambient temperature were determined to be 1.4 and 0.97, respectively (Fang et al., 2014). Fang et al. (2014) also demonstrated that the formation of ·OH and ·Cl was reduced by the decreased quantum yield at higher pH. On the other hand, OCl^- scavenges ·OH more rapidly than HOCl does. The rate constants of OCl^- and HOCl reacting with ·OH are 8.8×10^9 L/(mol · sec) and 2.0×10^9 L/(mol · sec), respectively (Connick, 1947; Matthew and Anastasio, 2006). The decreased removal efficiency of RR2 under alkaline conditions can be attributed to the above explanations. Earlier research on UV/chlorine oxidation of ronidazole demonstrated that the overall reaction rate and radical reaction rate of ronidazole decreased significantly as the pH increased owing to scavenging of ·OH by OCl^- (Qin et al., 2014). Further studies are required to clarify why UV/chlorine is more efficient in removing RR2 in neutral conditions than in acidic conditions.

2.3.3. Effects of inorganic salts
The changes of the RR2 concentrations and color during UV/chlorine oxidation in the presence and absence of inorganic salts, including NaCl and NaHCO₃, at pH 7 are shown in Fig. 7. Addition of NaCl and NaHCO₃ did not affect the removal of RR2 and color by UV/chlorine oxidation.
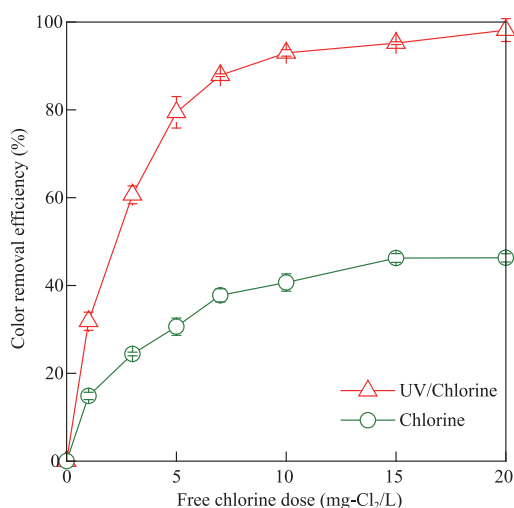

Fig. 5 – RR2 concentrations and color removal efficiencies during UV/chlorine oxidation with different doses of free chlorine at pH of 7. Initial concentration of RR2 20 mg/L, UV fluence rate 2.0 mW/cm², and irradiation time 6 min. RR2: C.I. Reactive Red 2; UV: ultraviolet.
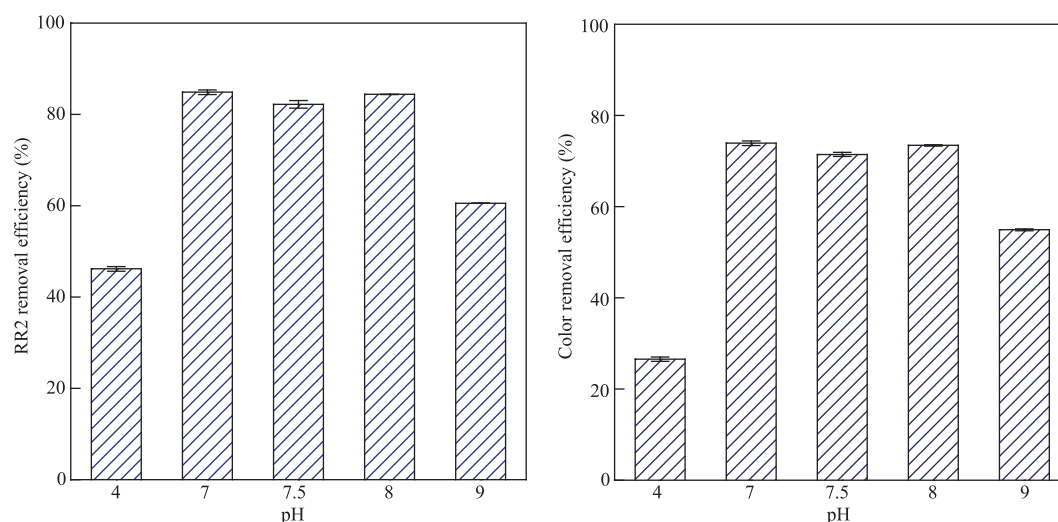
Fig. 6 – RR2 concentrations and color removal efficiencies after UV/chlorine oxidation at different pH values. Initial concentration of RR2 20 mg/L, free chlorine dose 5 mg/L, concentration of phosphate buffer 20 mmol/L, UV fluence rate 2.0 mW/cm², and irradiation time 6 min. RR2: C.I. Reactive Red 2; UV: ultraviolet.

Dye wastewater contains high concentrations of the anions HCO_3^- and Cl^-, which can reach levels above 0.6 g/L. In the present study, only limited effects of HCO_3^- and Cl^- on dye removal were found during UV/chlorine oxidation.

In this study, since addition of NaCl had little effect, Cl must play only a minor role in the degradation of RR2, with ·OH being predominant in enhancing RR2 degradation. During UV/H_2O_2 oxidation, ·OH scavenging effects were negligible at HCO_3^- concentrations lower than 0.3 g/L and Cl^- concentrations lower than 3.55 g/L. However, the rate of color removal for a reactive azo dye decreased at HCO_3^- concentrations higher than 0.3 g/L and Cl^- concentrations higher than 3.55 g/L (Gultekin and Ince, 2004). One study on the degradation of BA by a UV/chlorine advanced oxidation process found that the degradation efficiency remained constant as the Cl^- concentration increased (0 to 0.71 g/L), while increasing the HCO_3^- concentration (0 to 0.24 g/L) slightly reduced the BA removal rate by ·OH and significantly decreased the BA removal rate by ·Cl (Fang et al., 2014). These earlier results partly support the limited effect of HCO_3^- and Cl^- on RR2 removal in the present study.

2.4. Evaluation of electrical energy per order

There are a number of important factors in evaluating the feasibility of a wastewater treatment technology, including economics, regulations, effluent quality goals, and operation. Although these factors are all important, economics is often foremost. Since the UV/chlorine oxidation process is electric-energy intensive and electric energy typically represents a major fraction of the operating costs, simple figures-of-merit based on electric energy consumption can therefore be very useful (Daneshvar et al., 2005). The electrical energy per order of pollutant removal (E_{EO}) is a powerful scale-up parameter and a measure of the treatment rate in a fixed volume of contaminated water as a function of the applied specific energy dose (Bolton et al., 2001). Bolton et

al. (2001) reported that in the case of low pollutant concentrations, the E_{EO} (kWh/m³ per order) can be calculated from the following equation.

$$E_{EO} = \frac{P \times t \times 1000}{V \times 60 \times \log(C_i/C_f)} \tag{1}$$

where P is the rated power (kW) of the AOP system, t (min) is the irradiation time, V (L) is the treated wastewater volume, C_i and C_f (mg/L) are the initial and final pollutant concentrations.

Finally, it is useful to relate the E_{EO} values found in this study to treatment costs. For example, if the treatment objective for RR2 (initial concentration of RR2 = 20 mg/L) is 2 mg/L, the usage power is adopted as 8.5 W, the irradiation time is 10 min, and the volume of RR2 solution is 100 mL, this means that the total electrical energy required is 14.23 kWh/m³. If the cost of industrial electricity in China is 0.6 CNY/kWh, the contribution to the decolorization treatment cost from electrical energy will be 8.54 CNY/m³ of the wastewater.

3. Conclusions

The removal of RR2 and its color during UV/chlorine oxidation under different conditions was investigated, and the following conclusions were obtained:

(1) The combination of UV and chlorination resulted in a much higher removal rate of RR2 and its color than UV or chlorination alone. Increasing the chlorine dose increased the removal efficiency of RR2 and its color by UV/chlorine oxidation.

(2) Radicals, especially ·OH, played important roles in the enhancement of azo dye degradation by UV/chlorine oxidation.
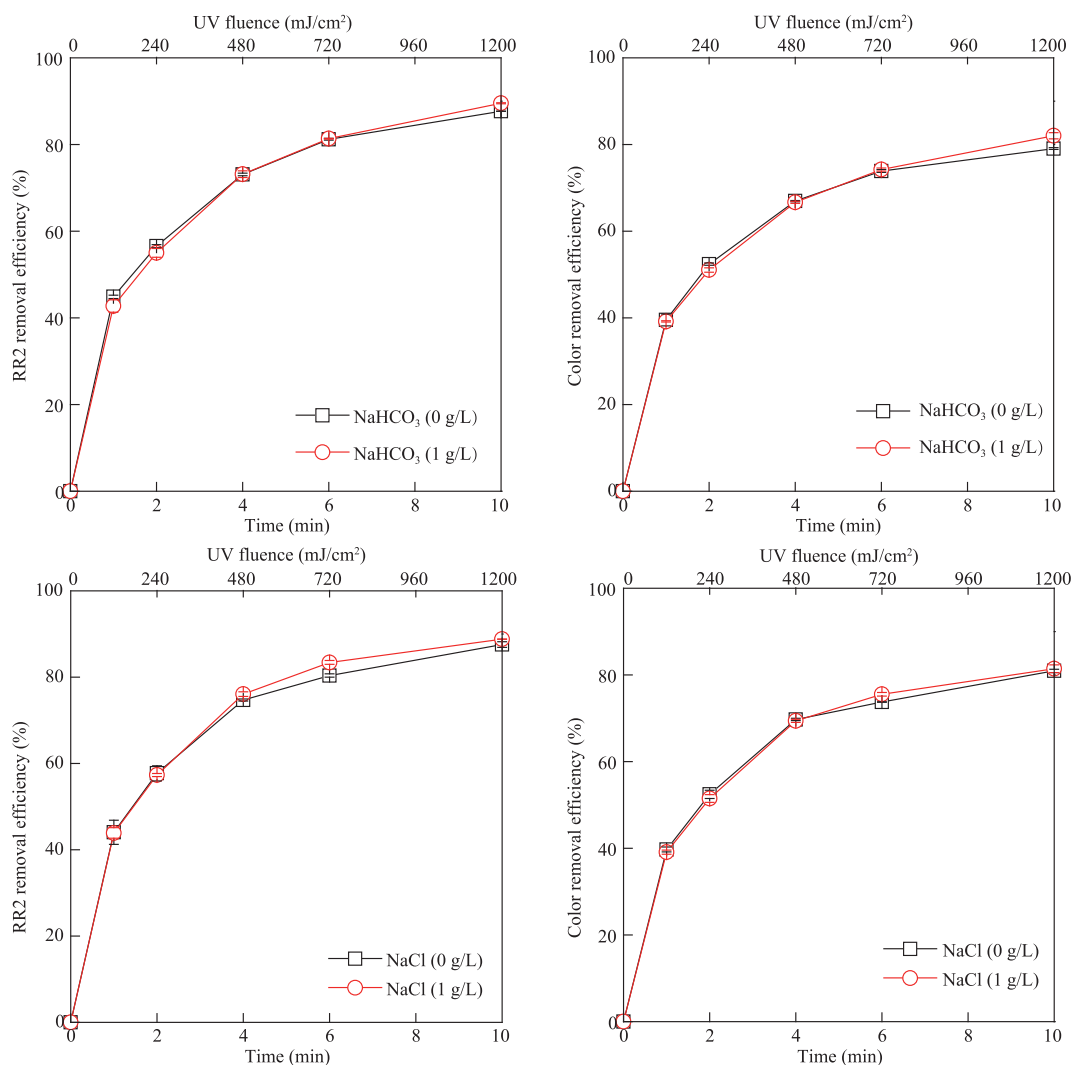
Fig. 7 – RR2 concentrations and color removal efficiencies after UV/chlorine oxidation of RR2 solutions with and without addition of inorganic salts. Initial concentration of RR2 20 mg/L, free chlorine dose 5 mg/L, pH 7, concentration of phosphate buffer 20 mmol/L, and UV fluence rate 2.0 mW/cm². RR2: C.I. Reactive Red 2; UV: ultraviolet.

(3) Higher RR2 removal was observed with UV/chlorine oxidation under neutral conditions than at pH 4 or 9.

(4) The presence of high concentrations of $NaHCO_3$ (1 g/L) and NaCl (1 g/L) had a limited effect on RR2 removal by UV/chlorine oxidation. This indicates that UV/chlorine is useful for azo dye solutions with high salinity.

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