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The fast decolorization of Reactive Red 31(RR31) dye solution by ceric ammonium nitrate (CAN)

Elham Keshmirizadeh[a,*], Hamid Modarress[b], Roghieh Didehkhani[a]

[a]*Department of Chemistry, Karaj Branch, Islamic Azad University, P.O. Box: 31485-313, Karaj, Iran, Tel. +98 26 34182305; Fax: +98 26 34418156; email: keshmiri@kiau.ac.ir (E. Keshmirizadeh), Tel. +98 26 34182318; email: golbarg500@yahoo.com (R. Didehkhani)*
[b]*Department of Chemical Engineering, Amir-Kabir, University of Technology, No. 424, Hafez Avenue, P.O. Box 15875-4413, Tehran, Iran, Tel. +98 21 6454 3176; Fax: +98 21 66405847; email: hmodares@aut.ac.ir*

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ABSTRACT

This paper examines the application of ceric ammonium nitrate (CAN) for fast degradation of Reactive Red 31 (RR31) dye in wastewater treatment. The results indicated that the removal of color and chemical oxygen demand achieved, respectively, was almost 99 and 92%. The parameters such as the amount of the added CAN, the initial pH 2–3, the initial dye concentration (10–1,000 mg/L), and decolorization time have been studied. The results show that CAN treatment of wastewater was more effective than the other advanced oxidation methods. The HPLC performance and UV–vis spectra confirmed the obtained results. The kinetics of decolorization reaction was estimated by half-life method and the order and rate constant of the reaction were evaluated.

Keywords: Dye decolorization; Reactive Red 31; Ceric ammonium nitrate; Degradation

1. Introduction

Cerium (IV) compounds are relatively moderate oxidizing reagents and less toxic in comparison with other oxidizing compounds [1,2]. Cerium (IV) salts with low toxicity are one-electron oxidizing agents [2]. Ceric ammonium nitrate (CAN) is an inorganic compound with the formula of $(NH_4)_2Ce\ (NO_3)_6$. CAN is an orange/red compound, which is soluble in water [3] and is greatly used as an oxidizing agent ($E \sim 1.61$ V) in organic synthesis [4]. In the redox reaction, Ce(IV) is converted to Ce(III), a one-electron change [2,5], resulting in the loss of the solution color from orange to a weak yellow [1]. CAN is useful as a powerful oxidant [5], especially for aromatics and dyes [6,7]. The main advantage of CAN over other cerium (IV) reagents is its higher solubility in water (1,410 g/L at 25°C) [1,3].

Dye wastewater is one of the most problematic industrial wastewaters to be treated. Large amounts of heavy colored wastewater are discharged from textile and similar industries which use many kinds of synthetic dyes. The complex aromatic structures of dyes make them persistent [8]. In addition, some dyes are either toxic or carcinogenic [9,10,11]. Traditional biological treatments were insufficient to completely remove color from effluents [12,13]. Although there are various methods for color removal, direct chemical oxidation (DCO) has become the method of choice because of its high efficiency and simple operation.

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*Corresponding author.

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Oxidation processes are greatly used in industrial treatment installations [14,15].

Application of cerium compounds in wastewater treatment has generally concentrated on the catalytic or catalytic assistance in the degradation of organic matter [16]; but, limited investigations have been performed on understanding the behavior of an individual cerium compound in wastewater treatment. However, it is evident that oxidation–reduction reaction occurs between Ce(IV) and the organic compounds in wastewater. Jianjun et al. [17] stated that in the hydrolysis of ceric sulfate, the complex $[Ce(OH)_y \cdot nH_2O]^{(4-y)+}$ is formed which has a large surface area and this species acts as an oxidizing agent. Although it is postulated that in hydrolysis of CAN at different solution pH, various species of Ce(IV) or Ce(III) are formed, but there is no report on the formation of other species.

In this paper, by considering the oxidizing properties of Ce(IV) in acidic media, the application of CAN through DCO of Reactive Red dye 31 (RR31) in wastewater treatment is investigated. The important operating parameters at ambient temperature in this study are: the pH, the amount of the added CAN, the initial dye concentration, and the reaction time. The results indicate that this method is easy and fast to be used for degradation of the RR31 dye in synthetic wastewater prepared in laboratory. The degradation kinetics is estimated by half-life method and the decolorization rate is fitted to a reaction rate equation with order of 0.7 with the correlation coefficient of $R^2 = 0.992$. Under the optimized conditions, the chemical oxygen demand (COD) decreases by almost 92% in the dye solutions. To confirm the obtained results and understand the behavior of the dye solution, the UV–vis spectra and the plot of HPLC performance are obtained and they are analyzed to substantiate the dye degradation results.

2. Materials and methods

2.1. Materials

Reagent grade of CAN (IV) (99%) obtained from Sigma–Aldrich, Germany, used as an oxidizing reagent and the Reactive Red 31 ($C_{30}H_{15}ClN_7Na_5O_{15}S_4$, MW: 992.14) from Alvan-rang Company, Iran, were obtained. The structure of the dye is presented in Fig. 1. It was used as received without further purification. Other chemicals used in the experiments were all of analytical reagent grade. A stock solution (1,000 mg/L) of RR31 was prepared and was suitably diluted in deionized water to the required initial concentration.

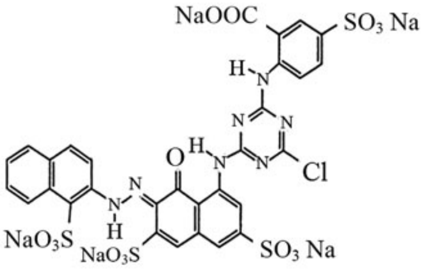

Fig. 1. Structure of the dye, Reactive Red 31 (RR31).

2.2. Batch study

In the direct oxidation process, CAN was used for oxidation of RR31 dye in a jar test in a batch reactor equipped with a magnetic stirrer and a heat bath to control the temperature. Oxidation process was carried out at 25°C. The literature search revealed that this oxidation process is exothermic in nature.

The experiments were performed in the following manner: firstly, the appropriate amount of CAN (concentration 0.05–0.7 mg/L) was added to the RR31 dye solution (concentration 10–1,000 mg/L), which was followed by pH adjustment to the desired value (2–10). Each experiment lasted 20 min. It was found that the optimum pH was pH 2–3.

2.3. Method

The mineralization and degradation were conducted in a 100-mL batch reactor. The initial pH of synthetic wastewater was regulated by NaOH (0.1 M) or H_2SO_4 (0.1 M). From a known concentration of CAN in the reactor, and at a constant stirring of 200 rpm (to homogenize the mixture), a sample of 10 mL was periodically withdrawn from the reactor at regular time intervals to follow the extent of mineralization and degradation with time. Finally, the reaction was terminated by spiking the sample with NaOH (1 M), which adjusted the pH at 9 ± 0.1 in order to prevent further generation of hydroxyl radicals. This consequently resulted in cerium hydroxide $Ce(OH)_3$ precipitation, which was filtered using 0.45-μm filter, and subsequently analyzed for the COD by obtaining UV–vis spectra and HPLC performance plot.

The concentrations of the dye solutions were followed by UV–vis spectrophotometer (Hach, Lange Model: DR-2800). A calibration curve for absorbance vs. concentration was constructed at the maximum absorbance (wavelength 522 nm). The standard method of wastewater measurements was used as recommended in Ref. [18]. HPLC analyses were performed using HPLC/Agilent/1100 to follow the progress of degradation. The HPLC stationary phase was an XDB-C18 column (150 mm × 4.6 mm), obtained at 30˚C and pH 2.0. The batch experiments were repeated and the results had the reproducibility within an error range of 3%.

The elimination percentage of dye was calculated from the following equation:

$$\text{Dye elimination } (\%) = \left(\frac{C_i - C_e}{C_i}\right) \times 100 \quad (1)$$

where C_i and C_e are, respectively, the initial and final (equilibrium) concentrations of the dye (mg/L).

3. Results and discussion

3.1. Effect of important operating parameters

In this study, the removal of RR31 was controlled by several operational parameters, such as the amount of CAN, the initial pH, the initial dye concentration, and the reaction time. The influence of these parameters was studied and explained in the following sections.

3.2. Direct oxidation of RR31 with CAN

The color of RR31 solution turns from red to weak yellow immediately after CAN was added to the solution, which indicates that RR31 has been oxidized. The spectra of RR31 demonstrated that after CAN was added, the structure of RR31 has been changed and no absorbance peak appeared in the range of 522–200 nm, which proves that RR31 has been depredated due to the addition of CAN and chemical reaction by cerium ions and hydroxyl radicals [1,19,20].

3.3. The amount of oxidant (CAN)

The aim of the preliminary tests was to find the optimum amount of CAN to be used for the studied wastewater, therefore the amount of CAN in the tests was varied from 0.08 to 0.65 g/L (or 0.0001–0.0011 Equivalent/L), respectively, for the initial dye concentration ranging from 10 to 1,000 mg/L, respectively. The results indicated that the percent of dye elimination increased as the amount of CAN increased. The results are presented in Fig. 2, as an example, for the initial dye concentration of 50 mg/L and for the reaction time completion of 30 s. Our search of the literature led to no findings on the application of CAN for removing textile dye such as RR31. However, Gozmen et al. [21] reported 98% degradation of Reactive Blue 4 using 2 g/L TiO_2/IO_4^- after 30 min illumination by UV light.

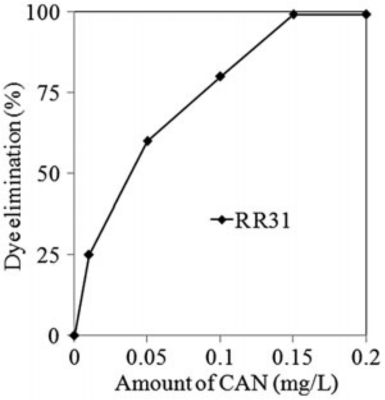

Fig. 2. Effect of CAN concentration on the dye elimination (%), at pH 2–3, initial concentration of the dye solution = 50 mg/L, volume of wastewater = 50 mL, and reaction time = 30 s.

3.4. Effect of initial pH

It has been proved that the initial pH of effluent is a prominent parameter influencing the performance of the dye removal process. The results in this study revealed that when pH of the dye solutions was less than 3, maximum color removal efficiency was observed. Fig. 3 demonstrates the effect of pH on the removal of RR31 dye from wastewater. These results show that the oxidation rate increases as the pH decreases and the percent elimination of the dye is about 96–99%, which is achieved within 30 s in the pH range of 2–3. Thus, an acidic pH would result in

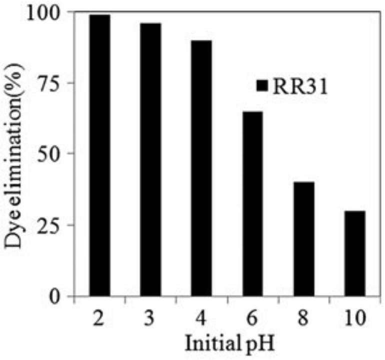

Fig. 3. Effect of pH on the dye elimination (%), at an initial concentration of dye solution = 50 mg/L, concentration of CAN = 0.15 g/L, volume of wastewater = 50 mL, and reaction time = 30 s.

more dye removal from the studied synthetic wastewater. By considering these results, it can be suggested that the oxidation reaction of the RR31 dye by CAN is a hydrogen ion catalyst reaction and the reaction has its highest rate at the optimum pH of 2–3. The rate of oxidation reaction will be discussed in Section 3.6, dealing with the decolorization kinetics of RR31.

To explain the observed kinetics of the dye removal, it can be postulated that, with hydrogen ions as catalyst, normal nonreactive CAN is transformed reversibly into an active form, with unknown nature. Then this unknown intermediate compound reacts with the dye molecule. This explanation has been presented by Jianjun et al. [17] and Keshmirizadeh and Dideh khani [22] for the decolorization of industrial wastewater by ceric sulfate. Also Hsueh et al. [23] used the same postulation to explain their obtained results for degradation of azo dyes in the Fenton and Fenton-like systems.

3.5. Effect of initial dye concentration

The dye solutions with different initial concentrations ranging from 10 to 1,000 mg/L were treated by direct oxidation at the optimized pH of 2–3 by adding the oxidant (CAN) for a given reaction time (20–75 s). The initial dye concentration and the concentration of CAN are presented in Table 1. According to the results in Table 1, up to the concentration of 300 mg/L, the rate of color removal (over 99%) is relatively constant. However, above this concentration, the dye elimination percent decreases to 96% for 1,000 mg/L of the dye in the given time 75 s. The possible explanation that can be presented is that at higher initial concentration of the dye, more anions are generated which compete with the dye to react with $^{\bullet}$OH radicals. These results and the explanations are consistent with those reported in the literature [24,25].

3.6. Decolorization kinetics of RR31

The half life of the reaction expressed as $t_{0.5}$ is the time needed for the concentration of the reactant to drop to one-half of its original value. For the following reaction:

$$\text{Dye} \xrightarrow{\text{Direct oxidation}} \text{Products} \tag{2}$$

The rate constant for this reaction is expressed as:

$$-r_{\text{Dye}} = \frac{-\mathrm{d}C_{\text{Dye}}}{\mathrm{d}t} = kC_{\text{Dye}}^{n} \tag{3}$$

After integration and mathematical manipulation of Eq. (3), the half life time will be obtained in the following form [26]:

$$t_{0.5} = \frac{(0.5)^{1-n} - 1}{k(n-1)} C_0^{1-n} \tag{4}$$

where the symbols in Eqs. (2)–(4) are defined as follows, r the rate of reaction, k the rate constant, n the order of reaction, C_{Dye} dye concentration at time t, C_0 is dye concentration at initial time ($t = 0$), and $t_{0.5}$ half life time. This expression exhibits that a plot of ln $t_{0.5}$ vs. ln C_0 is a straight line with the slope of $(1 - n)$, as shown in Fig. 4. The half-life method demands a series of experiments, with different initial dye concentrations and measuring $t_{0.5}$. As it is seen in Fig. 4, for $n = 0.7$, the slope of the line is positive.

The dye concentration in the solution was calculated from the absorbance data at the maximum absorbance

Table 1
Properties of initial synthetic dye wastewater based on optimum operating conditions for removal of RR31 by CAN (conditions: pH 2–3, volume of wastewater = 50 mL)

Initial dye concentration		Amount of CAN		
(mg/L)	(Equivalent/L)	(Equivalent/L)	Reaction time (s)	Dye elimination (%)
10	0.00001	0.0001	20	*>99
50	0.00005	0.0002	30	*>99
100	0.00010	0.0005	37	*>99
200	0.00020	0.0008	45	*>99
300	0.00030	0.0009	55	*>99
500	0.00050	0.0010	65	97
1,000	0.00100	0.0011	75	96

*>99: over 99%

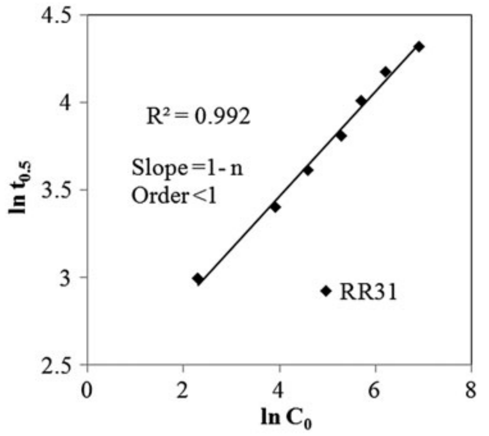

Fig. 4. Overall order of reaction from a series of half-life experiments, at different initial dye concentrations.

wavelength (522 nm) by the Lambert–Beer formula. The time dependence of each treated dye concentration was fitted to the following equation for $n = 0.7$,

$$C_{\text{Dye}}^{(1-n)} - C_0^{(1-n)} = (n-1)kt \tag{5}$$

where the resulting equation is expressed as follows:

$$C_{\text{Dye}}^{0.3} - C_0^{0.3} = 0.3kt \tag{6}$$

with the correlation coefficient $R^2 = 0.992$ and the rate constant is evaluated as: $k = 0.064\ ((\frac{\text{mg}}{\text{L}})^{0.3} \cdot \frac{1}{\text{s}}))$.

The decolorization results obtained in this study are reported in Table 1. Since, for kinetics of decolorization of RR31 no experimental data have been reported in the literature, a meaningful comparison with the other results cannot be presented; however, for most dyes, the available decolorization data indicates that the rate follows a first-order rate equation [27].

3.7. Mineralization of synthetic colored solutions

The mineralization of the RR31 solution with an initial concentration of 50 mg/L was used for direct oxidation with CAN in this study. This is a powerful process for degradation of dye since CAN has the ability to react selectively with aromatics, leading to high and fast color removal. In the present work, all the dye solutions were effectively decolorized after very short reaction time. To follow the mineralization (oxidation of the RR31 dye), UV–vis and HPLC [28] measurements were performed before and after adding CAN to the dye solutions. The results are presented in Figs. 5 and 6. As it is seen from Fig. 5, after adding CAN, the peak at the wavelength of 522 nm in the UV–vis spectrum has disappeared, which can be attributed to the decomposition of the dye. Also, the disappearance of absorbance peak at the wavelength of 254 nm which commonly indicates the presence of aromatic groups [29] in the dye has been fragmented.

The evolution of the UV–vis spectrum of the dye during oxidation with CAN in the acidic medium follows a similar trend as HPLC measurement represented in Fig. 6. As it is seen in this figure, after oxidation by CAN, the peak at retention time ($t_r = 1.062$ min) is an indication of the degradation of the dye. As it has been reported by other researchers, the disappearance of the HPLC peak of the dyes has been ascribed to the dye degradation [28–30].

3.8. COD removal

The extent of mineralization (or degradation) of the RR31 dye in the oxidation process by CAN in acidic solution (pH 2–3) can be evaluated by COD measurements. The COD measurements were done using the standard method, APHA–AWWA (method 5220B) [18]. The COD removal percent was calculated by the following equation:

$$\text{COD removal } (\%) = ((\text{COD}_0 - \text{COD}_t)/\text{COD}_0) \times 100 \tag{7}$$

where COD_t and COD_0, expressed in mg/L, are, respectively, the COD values at time (t) and at the initial time ($t = 0$). In the oxidation time of 30 s, the COD removal percent was evaluated as 92%, which indicates an effective mineralization of the RR31 dye by the oxidant

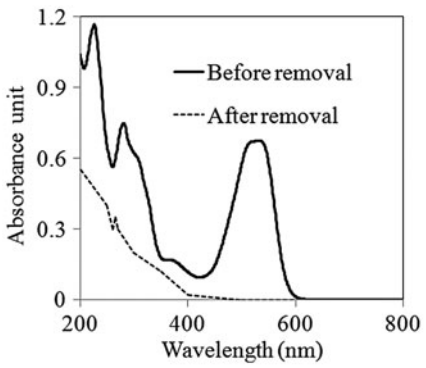

Fig. 5. UV–vis absorbance spectra of RR31 (Comparative curves before and after removal), at an initial concentration of dye solution = 50 mg/L, concentration of CAN = 0.15 g/L, volume of wastewater = 50 mL, and reaction time = 30 s.

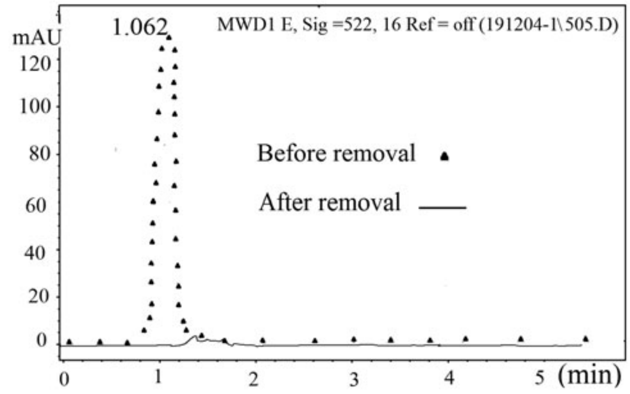

Fig. 6. HPLC spectra of RR31 (Comparative curves before and after removal), at an initial concentration of the dye solution = 50 mg/L, concentration of CAN = 0.15 g/L, volume of wastewater = 50 mL, and reaction time = 30 s.

agent CAN, compared with the reported COD removal of 90% in 30 min for the dye wastewater by Fenton oxidation [31] and COD removal of 70% for direct dyes by Fenton oxidation in 60 min [32].

4. Conclusions

This study demonstrated the application feasibility of the CAN for decolorization of the dye RR31. The results indicated that the dye removal efficiently was 99% in a short time. The concentration of the dye was varied from 10 to 1,000 mg/L and the optimum pH was 2–3. The results indicated that the oxidation of the dye resulted in faster decolorization and a maximum mineralization. The UV–vis, HPLC, and COD confirmed the results obtained by the RR31 dye oxidation by the CAN. The kinetics of dye degradation reaction was studied and it was found that the rate equation was of the order of 0.7. The results obtained in this work suggest that the oxidant CAN is as an effective decolorizing agent for RR31 dye. However, more studies are needed to understand the mechanism of oxidation process and to extend its application to decolorization of other dyes. We intend to pursue these studies in our future research and present the supporting results in the subsequent publications.

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