Journal of
Chemical Engineering & Process Technology

Yuksel, J Chem Eng Process Technol 2013, 4:9
DOI: 10.4172/2157-7048.1000179

Research Article Open Access

Hydrothermal Degradation of Congo Red in Hot Compressed Water and its Kinetics

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Abstract

A di-azo dye, Congo Red (CR) was used as a model compound to investigate the degradation mechanism in hot compressed water (HCW). The unique properties of HCW facilitated the degradation efficiency without addition of any organic solvent. The influences of reaction time, temperature, initial dye concentration and amount of hydrogen peroxide (H_2O_2) on the degradation of CR and the removal of total organic carbon (TOC) from the product solution were investigated. The presence of H_2O_2 was found to enhance the degradation of CR. The results showed that the degradation yield could reach 99.0% with a solution of 100 ppm CR and 50 mM H_2O_2 at 150°C at the end of 60 min. Maximum conversion of the total organic carbon was recorded as 62.2%. Moreover, the effect of the presence of several co-existing negative ions such as SO_4^{2-}, Cl^-, CO_3^{2-} were investigated. It was found that the presence of SO_4^{2-} accelerated evidently the degradation of CR. The other chosen anions (CO_3^{2-} and Cl^-) had an inhibitory effect on the decolorization of CR. Finally, kinetic study was carried out and the order of the reaction was calculated as 0.37.

Keywords: Congo red; Hot compressed water; Sub-critical water; Hydrothermal; Kinetics

Introduction

During the last decades, contamination of surface and ground water resources by various pollutant residues has become one of the major challenges for the preservation and sustainability of the environment. This contamination arises from surface runoff, leaching, wind erosion, deposition from aerial applications, industrial discharges and other sources [1]. Pesticides and heavy metal ions are one of the major threating groups of pollutants. Pesticides are among the most dangerous environmental pollutants because of their stability, mobility, capable of bioaccumulation and long-term effects on living organisms [2,3]. Removal of this kind of contaminants by adsorption [4-7], nanofiltration [8,9], using Fenton reagent [10], photo-catalytic degradation [11,12], biological treatment [13] and the combination of biological and photo-Fenton treatment [14] were widely studied. The other main contributors for environmental pollution are toxic heavy metals that are released from metallurgical, galvanizing, metal finishing, electroplating, mining industries [15]. Ion exchange resins [16-19], membrane filtration [20,21], adsorption [22-24], electrochemical [25] and biological treatments [26,27] are some of successful techniques for the removal of heavy metal ions (lead, arsenic, nickel, etc.) [28].

In addition to pesticides and heavy metal ions, textile dyes and other industrial dyestuffs constitute one of the largest groups of organic compounds that represent an increasing environmental danger [29,30]. About 10- 20% of the total world production of dyes is lost during the dyeing process and is released in the textile effluents [31]. This released colored wastewater creates serious environmental problems and can originate dangerous byproducts through oxidation, hydrolysis, or other chemical reactions taking place in the wastewater [32].

Organic dyes, particularly azo dyes, which contain one or more azo bonds, constitute one of the most important groups of pollutants in wastewater released from the industries such as textiles, paper, and leather [33,34]. These dyes are a major group of toxic, carcinogenic, colored and synthetic organic compounds [35,36]. Among azo dyes, in this study, it was given a special interest to a secondary di-azo dye Congo Red (CR) (sodium 3,3′ -(1E,1′ E)-biphenyl-4,4′-diylbis (diazene-2,1-diyl)bis(4-aminonaphthalene-1-sulfonate)). Because CR effluents are highly colored, have low biological oxygen demand (BOD) and high chemical oxygen demand (COD) while they contain high amounts of dissolved solids. Additionally, benzidine is a toxic metabolite of CR, which causes cancer of the bladder in humans [37]. The chemical structure of CR is shown in Figure 1.

The necessity of the removal of various types of dyestuffs has generated several studies in the last years including adsorption [38-40], ozonation [41,42], and photo-catalytic degradation [43-45] which are the most frequently used techniques for dye removal. However, these methods are inefficient and result in the production of secondary waste products that require further treatment.

Degradation of azo dyes by aerobic treatment is also not sufficient,

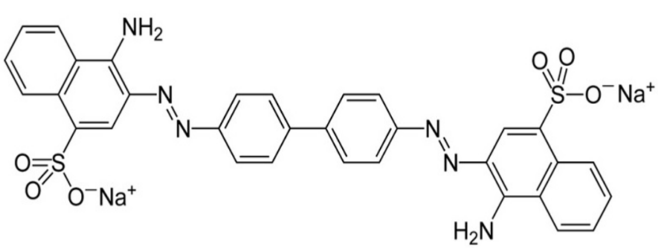
Figure 1: Chemical structure of the di-azo dye Congo Red (CR).

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Received November 06, 2013; **Accepted** November 28, 2013; **Published** November 30, 2013

Citation: Yuksel A (2013) Hydrothermal Degradation of Congo Red in Hot Compressed Water and its Kinetics. J Chem Eng Process Technol 4: 179. doi: 10.4172/2157-7048.1000179

and may even be toxic to activated sludge [46]. However, their color can be efficiently removed by an anaerobic step [47,48]. Anaerobic degradation yields only azo reduction, so that mineralization does not occur [49]. This often results in toxic and colorless aromatic amines, with mutagenesis and carcinogenesis potential [50].

Combined biological treatments (anaerobic, then aerobic), with some physicochemical pre-treatments are the most economical ways to decolorize dyed effluents to date [51]. However, textile process wastewaters are generally not concentrated enough for a methanisation stage to be efficient [49].

Chemical-oxidative processes mainly referred as "Advanced Oxidation Processes (AOPs)" have gained more attention recently. The principle of this method is the generation of hydroxyl radicals, one of the strongest known oxidant, to oxidize and mineralize organic molecule completely into CO_2 and inorganic ions. AOPs such as H_2O_2/UV processes, Fenton and photo-Fenton catalytic reactions [52-54] have been widely used to destroy organic pollutants [55]. In most cases, however, these techniques are not sufficient for the conversion of organic carbon in the liquid product solution to inorganic carbon such as CO_2 and CO.

At this point, hot compressed water (or sub-critical water) attracts attention with interesting properties: below the critical point, water behaves as an acid-base catalyst precursor. Additionally, the high relative static dielectric constant of 78.5 at 25°C drops to a value of about 6 at the critical point thus enhancing ionic reactions for the degradation of organic compounds [56]. Moreover, high solubility of organic substances and low viscosity make sub-critical water an excellent medium for fast, homogeneous and efficient reactions [57]. Depending on temperature and pressure, HCW supports either free radical or polar and ionic reactions, which means that HCW is a "tuning solvent" [58].

The main purpose of this work is to study the degradation of CR and removal of total organic carbon (TOC) from the liquid product solution by using HCW, which is clean, non-toxic, cheap and abundant, as a reaction medium without addition of any organic solvent. In order to optimize reaction conditions, effects of reaction time, temperature, initial dye concentration and amount of H_2O_2 as an external oxidant were investigated. Moreover, the effect of the presence of several co-existing negative ions such as SO_4^{2-}, Cl^-, CO_3^{2-} on both the conversions of dye and TOC were examined. Finally, kinetic study was carried out to calculate the order of CR degradation reaction and the rate constants by initial rate and integration methods.

Experimental Procedure and Analysis

Experimental apparatus and procedure

In this study, model dye wastewater was prepared by dissolving 100 ppm of CR in 100 mL of de-ionized water, at first without addition of any external oxidizer and then by adding 20 mM of H_2O_2 to increase the degradation efficiency of organic contaminants. Because of the fact that, in real textile effluents, dying stuff coexists with various amounts of salts, separate experiments were carried out by adding 1 g/L of different sodium salts (NaCl, Na_2CO_3 or Na_2SO_4) with and without H_2O_2. In the structure of CR, sodium is included so in order to clarify the effects of salt addition on the removal of both dye and TOC from the product solution, only sodium salts were preferred to avoid an extra pollution with different ions. Studied reaction temperatures were 120, 150, 175, 200 and 250°C. The reaction pressure and temperature profile for 250°C is given in Figure 2. To clarify the effect of oxidant addition, series experiment were done by the addition of 0, 10, 20 and 30 mM H_2O_2 and reactions were kept going for 30, 60, and 90 mins. For the kinetic study, calculations were done at three temperatures (120, 150 and 200°C) and initial CR concentrations (50, 100 and 125 ppm).

Degradation of CR in HCW was conducted by using a sealed 300-mL high temperature/high pressure batch reactor (Parr 5500, USA) made of SUS 316 stainless steel. In this system, the reactor vessel was made of titanium, which is quite well resistant to corrosion. Maximum temperature and pressure of the system were 350°C and 3000 psi, respectively. The batch reactor is illustrated in Figure 3. The model textile wastewater was prepared by adding 100 ppm (0.01 g) CR in 100 mL of de-ionized water in the titanium beaker (300 mL). For the experiments with external oxidizer, 20 mM H_2O_2 was added to the feeding solution. The experimental procedure described in Yuksel et al. [59], was applied for the hydrothermal degradation of CR.

Analytical methods

Acidity of the product solution was measured by a bench top pH meter (Thermo Scientific, Orion Star A111). In order to calculate dye

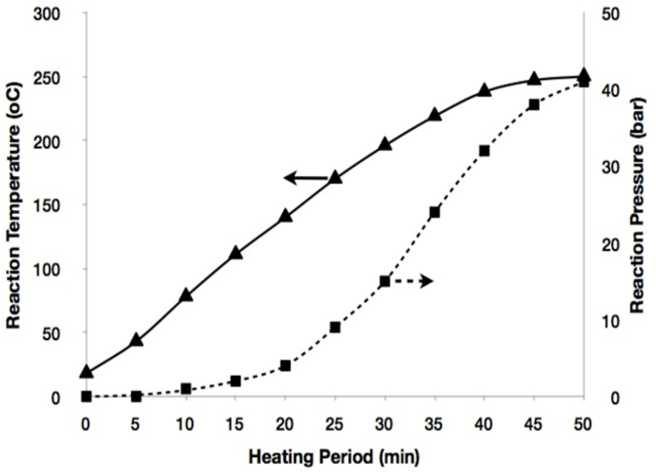

Figure 2: Typical temperature and pressure profiles for HCW at 250°C.

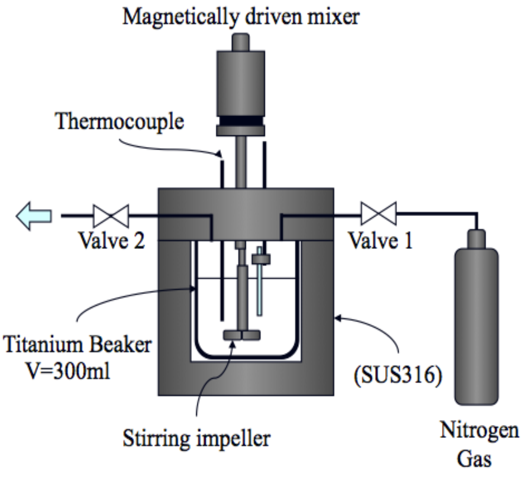

Figure 3: The experimental apparatus (batch reactor).

degradation, absorbance values were recorded between 200 and 800 nm using a scanning UV-visible spectrophotometer (Perkin Elmer, Lambda 45). Visible color removal from the product solution was measured at an optimum absorption wavelength of 499 nm.

The degradation percentage of CR was calculated based on the following Eq. 1:

$$\text{Degradation percentage (\%)} = [1 - (C_t / C_o)] \times 100 \qquad (1)$$

Where C_o (g/L) is the initial concentration of CR and C_t (g/L) is the concentration of CR at reaction time of t (min).

The organic and inorganic carbon content of the initial and final product solution were determined using a TOC analyzer (Shimadzu, TOC-VCPH). The instrument was operated using a 720°C furnace temperature by injecting 50 µL and 325 µL for total carbon (TC) and inorganic carbon (IC) measurements, respectively. It had a nitrogen-measuring unit (Shimadzu, TNM-1), which was used to determine the total nitrogen amount in the solution.

Results and Discussion

Effect of reaction temperature

The effect of reaction temperature (120, 150, 175, 200 and 250°C) on the removal of CR and TOC from the liquid product by using H_2O_2 as an external oxidant was investigated and experimental findings are represented in Figure 4. In these series of experiments, reactions were carried out with 100 ppm CR and 20 mM H_2O_2 for 60 min reaction time.

When reaction was carried out at 120°C, very small amount of dye (5.7%) was converted and most of the organic carbon (around 93%) was remained in the product solution. An increase in the dye degradation with rising reaction temperature was expected. On one hand, the collision frequency of molecules with the radicals increases when temperature rises. On the other hand, the fraction of molecules that possesses energy in excess of activation energy also increases; hence the dye degradation increases accordingly [60]. However, in this study, the conversion of CR at 150 and 250°C were almost same. It is deduced that the effect of reaction temperature was not significant to this reaction within the range studied. It may imply that the activation energy of the reactions could be very low. In this case, the main factor influencing the degradation mechanism was not temperature. It might be related to the concentration and life of radicals. In general, rise of temperature could help to vanish the active radicals. The negative effect of temperature on active species led to a decrease in the degradation percentage [61-64].

Because a lower reaction temperature is important for decreasing cost and increasing energy efficiency, the system temperature for the remainder of the experiments was set to 150°C.

In the case of TOC conversion, the highest efficiency was obtained at a temperature of 250°C. As shown in Figure 4, there was a significant difference in TOC conversions: at 120°C, it was measured as 7%, whereas at 250°C, 59% of TOC was removed from the product solution.

It must be pointed out that HCW at high temperatures has macroscopic properties like a non-polar solvent, but the single molecules are still polar. This change represents a new reaction medium that is suitable for organic species to be degraded [56]. Solubility of these non-polar substances in HCW is a consequence of temperature effect, which is directly related to entropy [61].

Reaction temperature also affects the formation of OH•. The life of this hydroxyl radical is very short and it was found that the decomposition rate of hydrogen peroxide increased with increasing reaction temperature. H_2O_2 decomposed very rapidly to the OH• that would rapidly attack to the dye molecule, leading to higher degradation rates.

Effects of oxidant (H_2O_2) concentration

To understand the role of an external oxidant on the conversion efficiency, separate experiments were carried out with different amounts of oxidant (0-30 mM) added to the model dying wastewater. For these experiments, H_2O_2 was used as an oxidant since it is strong and referred as an environmentally friendly oxidant with the oxidation byproducts of water and oxygen. Additionally, such strong oxidants can attack most of the organic structures found in the wastewater. In HCW, OH ions and radicals, which are responsible for the degradation of organic species (depending on temperature and pressure) have already been generated. With the addition of H_2O_2, the amount of these ions or radicals that would result in higher conversions is increased.

In these experiments, the temperature of the solution was adjusted to 250 and 150°C by heaters and the results are given in Figure 5. At first, reaction was carried out without any external oxidizer with a pH of 7.3. At 150°C, CR conversion was recorded as 6.8%, whereas at 250°C, it was 74.4%. When 10 mM of H_2O_2 was added to the feeding solution, a significant raise in the dye removal was noticed even at lower reaction temperature at a pH of 4.9. The dye conversion was increased to 89.6% from 6.8% at the end of 60 min. Similar trend was observed at 250°C, however, since the removal of dye from the product was already high without H_2O_2, the magnitude of the increase was not as high as it was at 150°C. When more H_2O_2 (20 mM) was used, CR conversion was found to be 99.0% at 150°C. With the increase in H_2O_2 amount to 30 mM (pH=4.4), it was observed that there was little bit decrease in CR conversion, which might follow a similar path for the addition of more H_2O_2 to the solution. In this study, the highest concentration of H_2O_2 was kept at 30 mM to avoid any risk of corrosion, since at HCW

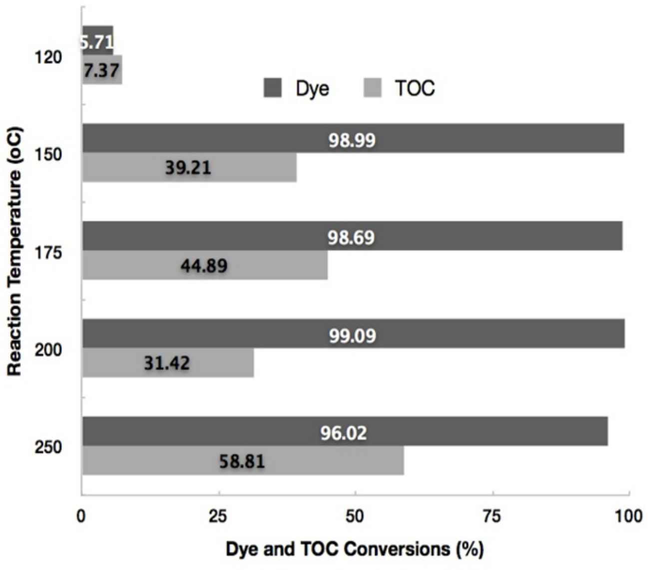

Figure 4: Effect of reaction temperature on the conversions of CR and TOC in the presence of 100 ppm dye and 50 mM H_2O_2.

because of high temperature and high pressure operating conditions; corrosion of the reactor is the common problem.

In the case of organic carbon removal from the product solution, TOC conversion was increased from 14.5% to 62.2% after the reaction with 30 mM H_2O_2 at 250°C. When the reaction was carried out at 150°C, resembling declination in TOC conversion was observed with a value of 34.3%. The reason of this decrease might be, with the addition of higher amounts of oxidant, more $OH^{\bullet}$ radicals are produced to attack the organic species in the structure of dye. However, when the hydroxyl free radicals are finally saturated with hydrogen peroxide, hydrogen peroxide is used more than hydroxyl free radicals to produce hydro peroxide ($HO_2^{\bullet}$). As well known, $HO_2^{\bullet}$ are less reactive than $HO^{\bullet}$, which explains well the decrease in the degradation yield with the addition of more H_2O_2. The hydroxyl radical propagation and termination involved are as follows [62-64]:

$$H_2O_2 + HO^{\bullet} \rightarrow HO_2^{\bullet} + H_2O$$

$$2HO^{\bullet} \rightarrow H_2O_2$$

$$HO_2^{\bullet} + HO^{\bullet} \rightarrow H_2O + O_2$$

$$HO^{\bullet} + \text{dye} \rightarrow \text{Products}$$

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$$HO_2^{\bullet} + H_2O_2 \rightarrow HO^{\bullet} + H_2O + O_2$$

As it can be clearly seen from Figure 6, the color removal was failed without H_2O_2 with the addition of 10 mM H_2O_2, decolorization was achieved but still it was insufficient. Finally, 20 mM H_2O_2 was found to be an optimum concentration for the best conversions of both dye and TOC.

Effects of reaction time and initial dye concentration

To investigate the effect of reaction time, experiments were done in 30, 60 and 90 minutes with the conditions of C_{CR}: 100 ppm; C_{H2O2}= 20 mM; reaction temperature: 150°C. The results are illustrated in Figure 7.

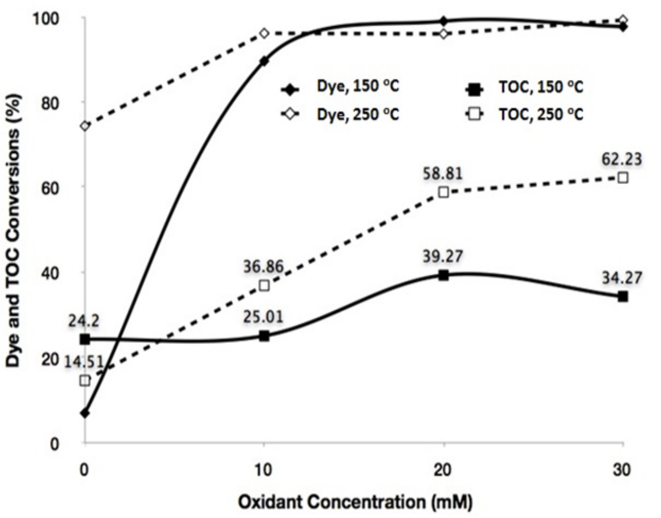

Figure 5: Effect of oxidant concentration on the conversions of CR and TOC at 150 and 250°C.

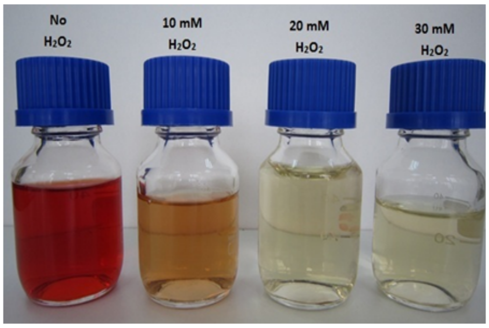

Figure 6: Product pictures after the treatment of 100 ppm CR with different amounts of H_2O_2 at 150°C.

According to Figure 7, after the treatment for 30 min, CR concentration reduced from 100 ppm to 25 ppm. When reaction was carried on for 60 and 90 min, the amount of CR were recorded as 0.9 and 1.1 ppm, respectively. As seen, almost all color (dye) disappeared at the end of 60 min. However, in the case of TOC conversion, longer reaction time (90 min) resulted in the removal of more organic carbon from the model wastewater with a value of 60.7%. This result indicates that the reaction trend was as follows: CR degraded initially resulting to intermediate products (containing aromatic rings) which in turn were further decomposed into simpler products till complete degradation to CO_2, water and inorganic salts.

In the decolorization of the aqueous solutions, TOC removal is as important parameter as the disappearance of the dye compound. After most of the treatment methods, although all color was almost removed from the wastewater, still significant amount of organic carbon remained in the productsolution. TOC conversion efficiencies are quite high in advanced oxidation processes based on the formation of $HO^{\bullet}$. In one study, the authors tried to degrade CR by galvanostic electrolysis and ozonation under similar conditions. They achieved around 85% of TOC removal by ozonation and by galvanostic electrolysis, almost complete mineralization occurred [65]. In another study, the mineralization of CR was done by decomposing ozone to the form of radical species with a very strong oxidation potential. Hence, both ozone and/or the free radicals broke the double bonds in the conjugated chains of the dye molecule. However, efficient mineralization had not been achieved with a TOC removal of 32% [41]. Seven azo dyes including CR (di-azo dye) were photo-catalytically degraded in TiO_2 suspension by Tanaka et al. [66]. 75% elimination of TOC was recorded after such a long reaction time of 240 min. The photo-catalytic degradation of azo dye proceeded predominantly through the oxidation by radicals and reduction by conduction band electron and electron injection from dye to conduction band. Same amount of conversion was achieved at 57 min for Acid yellow 17 (mono-azo dye) in the same study. As the number of azo bonds increased, the level of TOC conversion decreased because of the large dye molecules being broken down to small organic compounds for the same reaction conditions.

Figure 8 presents evolution with time of UV-vis spectra during hydrothermal degradation of dye wastewater contaminated with 100 ppm (0.1 g/L) CR for 30, 60 and 90 min. The reduction of CR characterized by the absorbance peak at 499 nm, clearly disappeared after 60 min. Although the absorbance at 499 nm decreased rapidly to near-zero level, the level of residual TOC was significant before 60 min. This behavior might be explained by considering that the active radicals and/or ions formed from water itself and H_2O_2 decomposition

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quickly attacked the azo dye, but the remainder of the molecule was not directly oxidized [67-70].

Bands situated in UV region of spectra can be attributed to π --π* transition in aromatic rings but the band of visible region can be due to azoic group transition. As it can be seen from Figure 8, continuous and simultaneous decrease of the band intensities was observed from the beginning of reaction in sub-critical water. These bands disappeared after 90 min. Total disappearance of the three bands (240, 340 and 499 nm) suggested that no more aromatic intermediates existed in the water. These results showed that total degradation of CR and its aromatic intermediates had been achieved by hydrothermal degradation [65]. At the first 30 min, CR started to decompose into aromatic intermediates. However, the degradation of these aromatic intermediates was not immediately started after they were formed, that could be proved with an increase in intensities of UV bands. After 60 min, almost complete destruction mechanism of azoic groups was involved and the degradation by-products absorbed at the same wavelengths with the initial compound [65].

The decolorization for CR was investigated at initial dye concentrations ranging from 50 ppm to 125 ppm at 150°C with 20 mM H_2O_2 concentration. It was clearly seen that with an increase in the initial dye concentration, removal of dye and total mineralization efficiency decreased. With 50 ppm initial concentration of CR, the color was successfully removed with a TOC conversion of 47%. Under the same reaction conditions, addition of 125 mM of dye resulted in a decrease in the conversions of both dye and TOC to 85% and 32%, respectively.

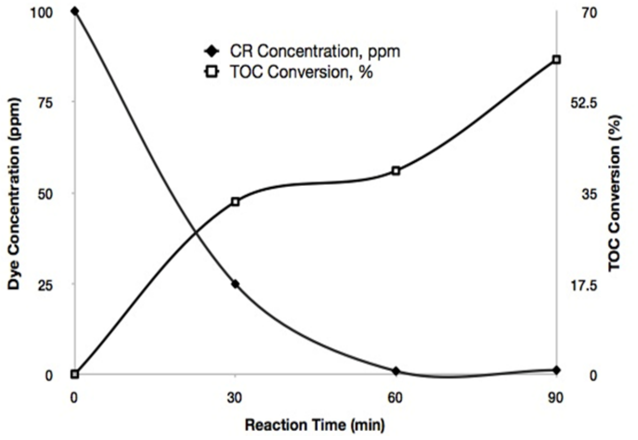

Figure 7: Effect of reaction time on the degradation of CR and TOC removal at 150°C.

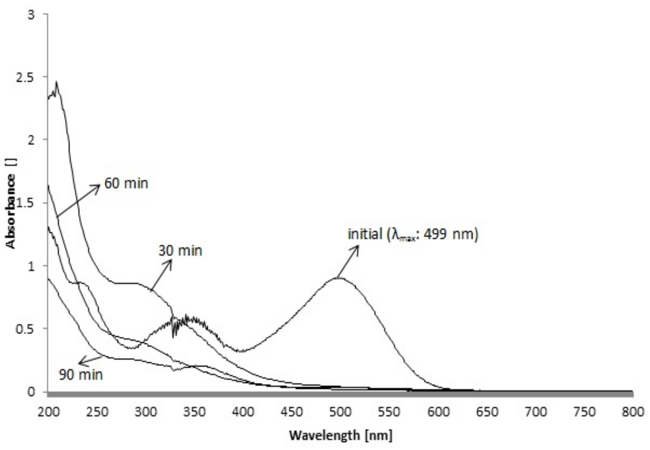

Figure 8: UV-visible spectra of the product solution at the end of 30, 60 and 90 mins. at 150°C.

This may be explained by the fact that, under hydrothermal condition, some radicals are generated; however, the active radical species have a nonselective property, which results in an attack on intermediate compounds produced rather than on the initial dye molecule while increasing the initial dye concentration [71]. Hence, the higher the concentration, the stronger the competition between the initial reactant and the intermediate products with active species. Such competition would be more pronounced in the presence of a high concentration level of reaction intermediates produced by the degradation of an increased initial dye concentration.

Effects of coexisting negative ions

In industrial wastewater, especially textile effluents, large amounts of inorganic salts are present with the dyes. Therefore, in this section, it was attempted to evaluate the influences of coexisting negative ions (SO_4^{2-}, Cl^-, CO_3^{2-}) on the degradation of CR and total mineralization efficiency at 150°C, at first without an external oxidizer, then with the addition of 20 mM H_2O_2. For this purpose, 1 g/L of NaCl, Na_2CO_3, and Na_2SO_4 salts were added to the model wastewater. Results of salt experiments are illustrated in Figure 9.

In the absence of H_2O_2, the addition of different sodium salts increased the decolorization rates of dye by enhancing the degradation of CR. When hydrothermal removal of CR was carried out without H_2O_2, degradation efficiency was very low around 7%. With the addition of 1 g/L of Na_2SO_4, it raised to 31%. In another experiments, the CR conversion values were recorded as 33% and 52% with the addition of NaCl and Na_2CO_3, respectively. In all cases, sodium salts were used.

At pH 8-10, most of the selected anions inhibited the degradation of CR in sub-critical water, when the model dye wastewater was prepared with 100 ppm CR and 20 mM H_2O_2. The inhibition by inorganic salts of the degradation of CR at basic pH was in the following decreasing order: chloride > carbonate > sulfate with inhibition percentages of 55%, 25% and 2%. Most of the color was removed when the reaction was carried out without addition of salt (98.99%) and with 1 g/L of Na_2SO_4 (97.16%).

In the literature, the inhibition of the degradation efficiency in the presence of ions is often explained by the scavenging of $HO^{\bullet}$ radicals by ions [69]. For example, the reaction of CO_3^{2-} with $HO^{\bullet}$ can be explained by the following equations [70]:

$$CO_3^{2-} + HO^{\bullet} \rightarrow OH^- + CO_3^{\bullet -}$$

$$HCO_3^- + HO^{\bullet} \rightarrow H_2O + CO_3^{\bullet -}$$

The addition of Na_2SO_4 together with H_2O_2 had almost no influence on the degradation of CR. This might be explained by the reaction between SO_4^{2-} and $HO^{\bullet}$ under hydrothermal conditions.

$$SO_4^{2-} + HO^{\bullet} \rightarrow OH^- + SO_4^{\bullet -}$$

SO_4^{2-} formed from the equation above is less reactive than $HO^{\bullet}$ radicals, therefore although in this study the amount of salts used (1 g/L) did not create extreme saline conditions, if excess Na_2SO_4 salt was

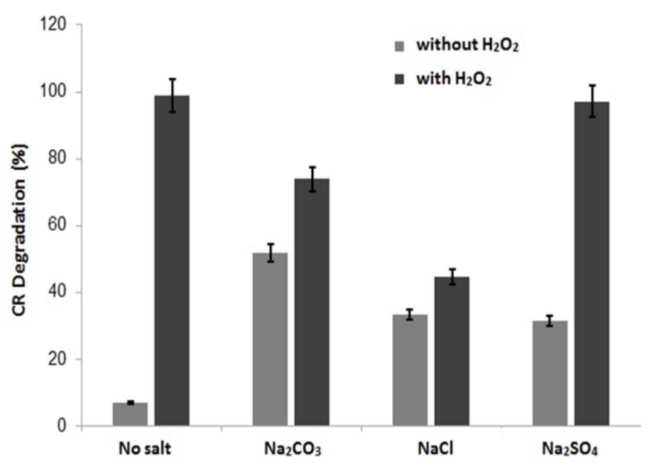

Figure 9: Effect of coexisting negative ions (SO_4^{2-}, Cl^-, CO_3^{2-}) on the degradation of CR with and without H_2O_2 at 150°C.

added, it would hinder the removal of color from the product solution [71,72].

The inhibitory effect of Cl^- was the highest (55%). As shown in Figure 10, the characteristic peak of CR at 499 nm corresponded to an absorbance value of 0.038 without any salt. This value increased to 0.52 with the addition of 1 g/L NaCl to the model wastewater, as an indication of the inhibitory effect of NaCl on the degradation of CR. This could be explained by the possible competitive reaction of Cl^- ions that could oxidize on the surface of reaction vessel made of titanium. In addition, at high temperatures, the mass transport controlled reduction of hypochlorite may be another reason for a decreased dye removal according to the following cathodic loss reaction [73,74]:

$$OCl^- + H_2O + 2e^- \rightarrow Cl^- + 2HO^-$$

The GC-MS analysis proved that no formation of secondary nitrogen containing organic pollutants was observed even in the presence of NaCl that showed the most inhibitory effect. The GC-MS spectrum of the model wastewater prepared by 100 ppm CR, 20 mM H_2O_2 and 1g/L NaCl and treated at 150°C for 60 min, is given in Figure 11.

In azo dyes, both nitrogen atoms are already formally at the zero oxidation degree. In the initial model wastewater, this oxidation degree favors the evolution of gaseous di-nitrogen with being close to zero combined with the existence of a –N=N– double bond [70]. N_2 evolution constitutes the ideal case for a decontamination reaction involving totally innocuous nitrogen-containing final product. Although in this study, GC-TCD analysis was not done, the results of GC-MS and TN analysis confirmed that, when the conversion of dye was high, almost complete mineralization was achieved.

Kinetic study

For the kinetic analysis, initial rate and integration methods were used. For the initial rate method, the reaction was carried out with different initial concentrations of CR (0.05, 0.1 and 0.125 g/L) at a reaction temperature of 150°C, whereas, for the integration method, initial concentration of CR was kept constant at 0.1 g/Land the final concentrations of CR were measured for different reaction times (30, 60 and 90 min).

For the initial rate method, following procedure was applied:

From the definition of rate: $-r_A = \frac{NAo}{V} \times \frac{dx}{dt}$ (2)

can be written. If conversion (x) vs time (t) was plotted, its slope at t=0 would give the $\left(\frac{dx}{dt}\right)$. Using Eq. 2, initial rate could be calculated. Figure 12 presents x vs t curves for different initial concentrations of CR (50, 100 and 125 ppm).

Calculated $(-r_A)_o$ values are given in Table 1.

For nth order reaction rate, rate expression is given by Eq.3: -rA0 = k (3)

Taking logarithm of both sides, the following Eq. 4 was obtained:

$$\ln(-r_{A0}) = lnk + nlnC_{A0} \quad (4)$$

From the slope of $\ln(-r_{A0})$ vs lnC_{A0} graph, the reaction order (n) was calculated as 0.38.

The order of reaction was also calculated from the integration method as follows:

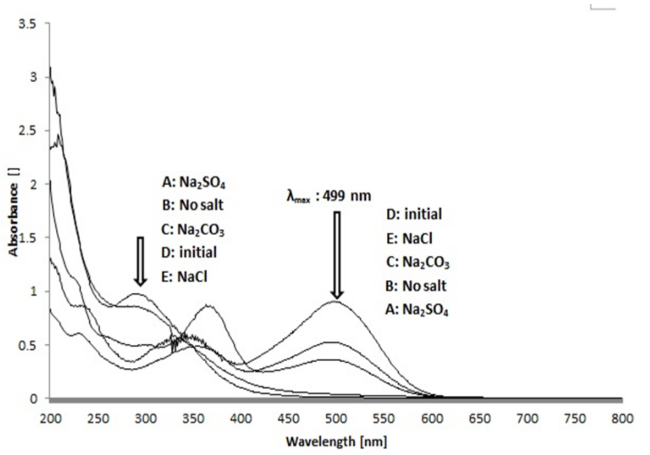

Figure 10: UV-visible spectra of the product solution with 1 g/L of NaCl, Na_2CO_3, and Na_2SO_4 salts at 150°C.

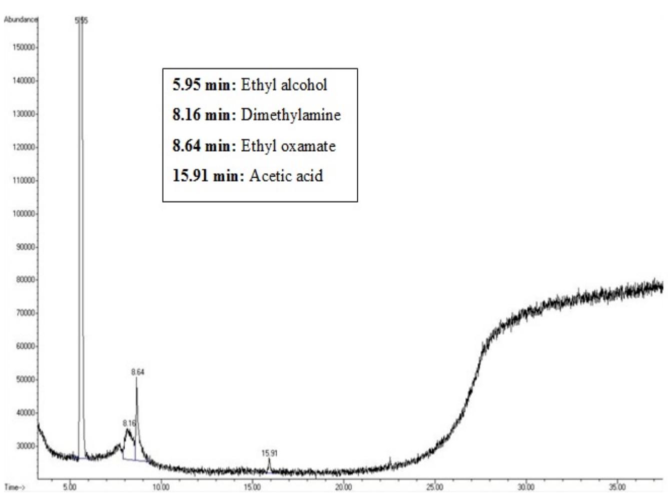

Figure 11: GC-MS spectrum of the model dye wastewater (CR concentration: 100 ppm; salt addition: 1 g/L NaCl; oxidant concentration: 20 mM H_2O_2; reaction temperature: 150°C; reaction time: 60 min).

$$-\frac{dN_A}{dt} = r_A V \tag{5}$$

For constant volume batch reactor, Eq. 5 becomes:

$$-\frac{dC_A}{dt} = r_A = kC_A^n \tag{6}$$

where C_A is the final concentration of CR in the product solution, t is the reaction time, k is the rate constant and n is the order of reaction. When Eq. 6 is integrated, the final form of the equation for the calculation of n becomes:

$$\ln C_A = \left[\frac{\ln(1-n)}{n-1} + \frac{\ln k}{n-1} + \ln C_{A0}\right] + \left(\frac{1}{n-1}\right)\ln t \tag{7}$$

This expression $\left[\frac{\ln(1-n)}{n-1} + \frac{\ln k}{n-1} + \ln C_{A0}\right]$ in Eq. 7 was a constant value. By the integration method, after drawing $\ln(C_A)$ vs $\ln(t)$, the order of reaction was calculated as 0.36. The calculated value was 0.38 from the initial rate method. Since two values were very close to each other, for the rest of the kinetic study, the mean value, which was **0.37**, was taken as the order of the degradation reaction of CR in sub-critical water.

For the calculation of reaction rate constants (k), reaction was carried out at three different temperatures of 120, 150 and 200°C. From the definitions of rate and conversion, Eq. 8 was obtained.

$$\frac{C_{A0}^{1-n}\left[(1-x)^{1-n}-1\right]}{n-1} = kt \tag{8}$$

Since n was calculated as 0.37 and C_{Ao} was 100 ppm (1.435×10^{-4} mol/L), this expression can be written as:

$$-6.018\times10^{-3}\left[(1-x)^{0.63}-1\right] = kt \tag{9}$$

If the expression in the left hand side of Eq. 9 was plotted against time, k values at each temperature could be calculated from the slope. The conversion and k values at different reaction times can be seen in Table 2.

From Table 2 it was observed that, at 120°C, the color was decreasing relatively slowly with a rate constant of 0.0012 $(\mathrm{mol/L})^{0.63}\mathrm{L}^{-1}$.

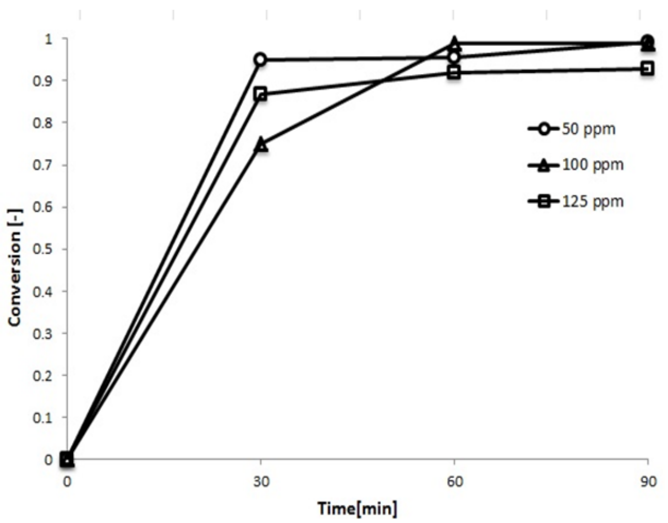

Figure 12: Conversion values of CR with the initial concentrations of 50, 100 and 125 ppm at 150°C.

C_{A0} (ppm)	$C_{A0}\left(\frac{mol}{L}\right)$	$\left(\frac{dx}{dt}\right)_{t=0}\left(\frac{1}{min}\right)$	$(-r_A)_0\left(\frac{mol}{Lmin}\right)$
50	7.177×10^{-5}	-2.8654	2.0565×10^{-4}
100	14.35×10^{-5}	-1.539	2.2162×10^{-4}
125	17.94×10^{-5}	-2.4561	4.4062×10^{-4}

Table 1: Calculated initial rates $[(-r_A)_o]$ for 50, 100 and 125 ppm CR at 150°C.

	120 °C	150°C	200 °C
t (min)	*x*	*x*	*x*
30	0.79	0.7516	0.8414
60	0.8157	0.9899	0.99091
90	0.8012	0.98889	0.9277
$k\left(\frac{mol}{L}\right)^{0.63}(min^{-1})$	**0.0012**	**0.0016**	**0.0015**

Table 2: Calculated conversions (x) and reaction rate constants (k) at 120, 150 and 200°C.

As temperature raised to 150°C, reaction rate constant increased to 0.0016 $(\mathrm{mol/L})^{0.63}\mathrm{L}^{-1}$, as expected. However, high temperature does not always result in a higher reaction rate. Due to the mass transfer limitation of H_2O_2 at 200°C, rate constant dropped to 0.0015 $(\mathrm{mol/L})^{0.63}\mathrm{L}^{-1}$ at this temperature.

Conclusions

The degradation of Congo Red (CR) as a model compound of di-azo dyes was studied in hot compressed water without any organic solvent under various operating conditions by using an autoclave. In the presence of 20 mM H_2O_2 as an external oxidant, at 150°C, 99% of CR was successfully removed from the model dye wastewater at the end of 60 min. The maximum amount of TOC conversion was recorded as 62%. From series of experiments, it was observed that the amount of external oxidant greatly affected the degradation of dye itself and TOC conversion. Without H_2O_2, only 7% of CR and 24% of TOC conversions were recorded after 60 min, respectively. The effect of the presence of several co-existing negative ions such as SO_4^{2-}, Cl^-, CO_3^{2-} on both the conversions of dye and TOC were also investigated and found that the presence of SO_4^{2-} accelerated evidently the degradation of CR, while the other CO_3^{2-} and Cl^- anions had an inhibitory effect on the decolorization of CR with the inhibition percentages of 25% and 55%, respectively. Finally, kinetic study at temperatures of 120, 150 and 200°C was carried out and the order of the reaction was calculated as 0.37 as a mean value from the initial rate and integration methods. Under optimum conditions (reaction temperature: 150°C; oxidant amount: 20 mM; reaction time: 60 min), the rate constant (k) was calculated as 0.0016 $(\mathrm{mol/L})^{0.63}\mathrm{L}^{-1}$. The results proved that without any organic solvent, as a green technology, water itself could be a good reaction medium for the degradation of organic contaminants by just tuning its temperature and pressure.

Acknowledgements

Izmir Institute of Technology (IZTECH) Scientific Research Committee supported this work with a project number of 2012IYTE01. I would like to thank to Filiz Kurucaovali, Fatma Ustun and Belgin Tuncel for their help in TOC and UV analysis of the product solution.

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