

Electrolytic Treatment of Azo Dye Wastewaters: Impact of Matrix Chloride Content

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Abstract: Direct Red 83 (10 μM) was electrolytically treated with a graphite anode paired with a stainless steel cathode at 0.05 mA/mm². Electrolyte composition was varied from 0 to 0.05 N sodium chloride in increments of 0.01 N, using sodium sulfate as a makeup salt to keep the total electrolyte strength at 0.05 N. Fraction of dye remaining was plotted versus time, and first order curves were fitted to the data. Apparent first order rate constants ranged from 3.96×10^{-5} to $1.24 \times 10^{-3} \text{ s}^{-1}$. Both direct oxidation by applied current and indirect oxidation by electrolytically formed chemical species were responsible for color removal. The rate of indirect oxidation was slower than the rate of chlorinated oxidizing species production above 0.01 N sodium chloride concentration. Decolorization rate increased with increasing chloride concentration to a rate-limited point occurring at 0.04 N sodium chloride in the system studied.

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Introduction

Dyes are a highly visible contaminant in water, even at very low concentrations, <1 mg/L for some dyes. They can be difficult compounds to treat because of their synthetic origin and often complex aromatic molecular structures. In fact, the types of chemical structures that make a dye resistant to fading on exposure to sweat, soap, water, light, or oxidizing agents, also make the dye more stable and less amenable to biodegradation (Banat et al. (1996)). This presents a challenge to publically owned treatment works that typically rely on biological treatment systems and, as a result, most developed countries are passing more stringent legislation requiring the removal of dyes from industrial effluents prior to discharge. This is motivating research into alternative ways to pretreat these compounds; one such alternative is electrolytic treatment.

Research interest in the use of electrolytic treatment for the decolorization of dye and textile wastewaters has been increasing over the last several decades, but electrolytic decomposition of recalcitrant organic compounds—especially cyanides, phenols, and thiocyanates—in industrial wastewater has been the subject of research and patents since the 1950s (Kuhn 1971). The tech-

nique of anodic oxidation of wastes containing dyes was developed in the early 1970s based on research conducted in Japan (Abdo and Al-Ameeri 1987). Over the last few decades, several research groups (Abdo and Al-Ameeri 1987; Lin and Peng 1993; Ogutveren and Koparal 1994; Naumczyk et al. 1996; Jia et al. 1999; Davila-Jimenez et al. 2000) have shown that electrochemical treatment of dyes is possible in a variety of reactor configurations designed to emphasize different removal mechanisms such as direct oxidation, indirect chemical oxidation, or electrocoagulation/electroflocculation. It has been noted, though, that the presence of chloride in the waste stream has an impact on the rate of dye decolorization in an electrolytic system because it not only conducts electrons in the system to facilitate direct oxidation of the dye, but it reacts at the anode to form oxidized chlorine species that are capable of reacting with the dye to decolorize it via indirect oxidation (Chiang et al. 1995; Chiang 1997; Ogutveren et al. 1999).

The research described in this paper expands on the current knowledge base by examining the impact of matrix chloride concentration on the decolorization rate for a copper-complexed azo dye, Direct Red 83 (DR 83), shown in Fig. 1.

Materials and Methods

Dye Source and Preparation

Direct Red 83 [Fabrifast Rubine 3BLL; Chemical Abstract Service (CAS) Number 15418-16-3] was obtained from the manufacturer, Fabricolor Dyes and Pigments, Paterson, N.J. and purified to ~97% using a “salting out” method described by Vickerstaff (1954). Using this method, the dye was precipitated from hot concentrated aqueous solution by salting it out with sodium acetate. The precipitate was filtered, redissolved, and reprecipitated several times before the purified precipitate was extracted with boiling ethyl alcohol to remove the sodium acetate. After alcohol extraction, the remaining precipitate was collected and dried to remove the ethyl alcohol and any remaining moisture, resulting in a purified sodium salt of the dye.

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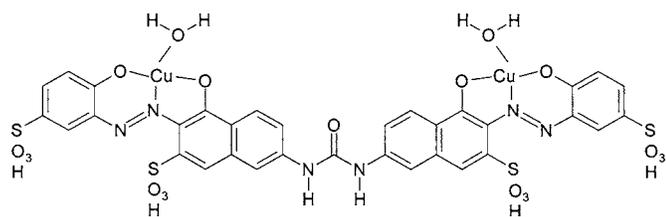


Fig. 1. Structure of Direct Red 83

Electrolyte Solutions

Stock electrolyte solutions were prepared were at a normality (N) of 1.5 equivalents per liter from American Chemical Society (A.C.S.) reagent-grade sodium chloride (NaCl , CAS No. 7647-14-5, Fisher Scientific, Incorporated) or sodium sulfate (Na_2SO_4 , CAS No. 7757-82-6, Mallinckrodt, Incorporated) in $>18\text{ M}\Omega$ purified water.

Experimental Apparatus

The experimental apparatus consisted of an electrochemical cell in circuit with a Model 362 scanning potentiostat (Princeton Applied Research EG&G Instruments) and a Keithley 179 TRMS digital multimeter with an isolated output option. This was interfaced with a computer data acquisition system (National Instruments Corporation GPIB-PCAI NI-488.2) as shown in Fig. 2.

The electrolytic cell was a 500 mL glass jar with a Teflon-lined lid. The graphite anode and stainless steel cathode electrodes were 6.35 mm diameter rods cut in 98.5 mm lengths made from graphite (99% metals basis, Alpha Aesar) and stainless steel (Type 303, Fe:Cr:Ni 73:18:9% by weight; Alpha Aesar) stock, respectively. Each rod was inserted through a grommet in the lid until the electrode just missed touching the bottom of the cell (85 mm into cell). A 250 mm length of 18 gage hookup wire (Number 278-1226, Radio Shack, Tandy Corporation, Fort Worth, Tex.) with a 6.35 mm internal diameter (i.d.) ring terminal (Number 70009, Buchanan Construction Products, Incorporated, Hackensack, N.J.) soldered to it was slipped over the portion of the rod above the cell lid and held in place with a 6.35 mm rubber screw protector (Crown Bolt, Incorporated, Cerritos, Calif.). The silver/silver chloride (Ag/AgCl) reference electrode (Bioanalytical Systems, Incorporated, West Lafayette, Ind.) was plugged into

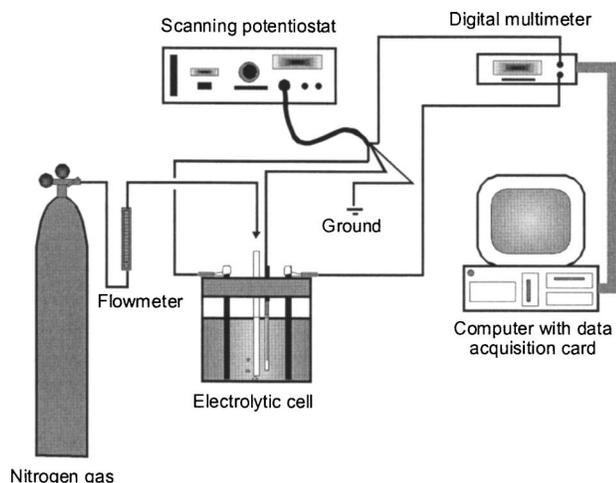


Fig. 2. Overview of experimental apparatus

the socket in the lid, and a piece of glass tubing (63 mm i.d. \times 120 mm) was inserted through the lid until the tip just missed touching the bottom of the cell. The electrolytic cell was mixed using compressed nitrogen (PP grade, Wright Brothers, Incorporated, Cincinnati) with the flow rate controlled using a two-stage regulator (Fisherbrand Model No. 10-572-D, Fisher Scientific Company) and measured with a flow meter (Precision Bore Flowrator Tube No. 2-L-150/13, F. & P. Company) Tygon-R-3603 6.35 mm i.d. tubing was used to connect the regulator, flow meter, and glass tube inserted through the lid of the cell.

Experimental Method

The test solution was prepared by diluting 20 mL of a concentrated stock solution of the Direct Red 83 dye (150 μM to 100 mL and adding it to the electrolytic cell jar. The electrolyte composition varied from 0 to 0.05 N NaCl in 0.01 increments. The salts were added to the cell as 0, 2, 4, 6, 8, or 10 mL of a 1.5 N NaCl stock plus 10, 8, 6, 4, 2, or 0 mL, respectively, of a 1.5 N Na_2SO_4 stock diluted to 100 mL with purified water. The cell contents were diluted to 300 mL with purified water to provide a total electrolyte concentration equal to 0.05 N and a DR83 concentration equal to 10 μM .

A new graphite anode was used for each run, paired with a stainless steel cathode electrode that was thoroughly buffed with fine gage steel wool and sand paper and cleaned with purified water ($>18\text{ M}\Omega$) prior to the run. Nitrogen gas at 0.0028 st. in.³/min was used to mix the reactor contents. Sample conductivity, pH, and temperature were measured before and after each run on samples from the bulk reactor. Two 5 mL subsamples were collected from the reactor at each of seven sampling times (0, 600, 1,200, 1,800, 2,400, 3,200 and 3,600 s). One 5 mL subsample was added to a sample vial with one drop of a 2 M sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) solution to quench the action of any oxidizing chlorine species present in the sample and immediately stabilize the sample; the other 5 mL subsample was left unquenched and allowed to continue to react until active oxidizing species were no longer present (≥ 24 h). Both sets of subsamples were analyzed for absorbance spectra to calculate DR83 concentration as measured by absorbance at 533 nm. Data from the quenched samples reflected the amount of dye still present at the sample time; data from the unquenched samples were indicative of the amount of additional dye removal possible without the expense of additional electrical current. Chlorine residuals were measured immediately after 3,600 s of treatment (in samples with no dye color interferences only). The current supplied to the system was adjusted for the loss of usable electrode surface area due to sample removal in order to maintain a constant current density of 0.05 mA/mm^2 . The potential was noted periodically throughout the run.

Temperature and conductivity were measured using a Checkmate II meter equipped with a temperature sensor and a conductivity/total dissolved solids sensor (Corning Scientific Products). Conductivity was calibrated to a potassium chloride calibration standard of 1.288 mS/mm .

Solution pH was measured with a Fisher Scientific Accumet Research AR25 dual channel pH/ion meter equipped with a Ag/AgCl combination pH electrode.

Ultraviolet-visible (UV-VIS) absorbance spectra were measured using a Hewlett-Packard Model HP8453 UV-VIS diode array spectrophotometer with a 10 mm path length quartz cell. Absorbance readings in absorbance units (AU) were recorded at

Table 1. Summary of Conductivity, pH, Temperature, Chlorine Residual, and Potential Data

NaCl (N)	Na ₂ SO ₄ (N)	Conductivity (mS/mm)		pH (S.U.)		Temperature (°C)		Free chlorine residual (mg/L)	Potential (V)
		Initial	Final	Initial	Final	Initial	Final		
0	0.05	0.488	0.488	6.61	6.65	21.1	19.1	^b	2.8–3.0
0.01	0.04	0.498	0.502	6.27	^a	21.4	19.5	^b	~2.8
0.01	0.04	0.503	0.503	6.25	6.81	20.4	18.4	^b	2.7–2.8
0.02	0.03	0.514	0.515	6.22	7.00	21.0	18.8	^b	2.6–2.7
0.03	0.02	0.529	0.530	6.40	7.17	20.9	19.0	0.19	2.6–2.7
0.04	0.01	0.539	0.545	6.41	7.60	21.3	19.6	1.04	2.6–2.7
0.05	0	0.555	0.558	6.28	7.54	20.7	18.7	0.81	2.6–2.9

^aSample lost due to sample vial contamination.

^bNot available due to dye residual interference with analytical endpoint.

1 nm intervals over a range of 190–1,100 nm with an intergration time of 0.5 s. The spectra were downloaded into Microsoft Excel spreadsheet files.

Free and combined chlorine residuals were measured using 20 mL samples diluted to 100 mL with >18 MΩ water. A titrimetric method, Method 4500-C1 F (APHA-AWWA-WEF 1995), was followed using premade solutions from Lab Chem, Incorporated, including the N,N-diethyl-*p*-phenylenediamine indicator solution, potassium iodide solution, and ferrous ammonium sulfate titrant solution. The buffer solution was prepared using reagent grade sodium phosphate dibasic (Fisher Scientific S-374), potassium phosphate monobasic (Fisher Scientific P284-500), ethylene diamine tetra-acetic acid (ICN Biochemical), and mercuric chloride (Fisher Scientific MI55-50).

Results

A summary of the conductivities in mS/cm, pH values in standard units (S.U.), temperatures in degree centigrade (°C), chlorine residuals in milligram/Liter and potential ranges in volts (V) for each run is given in Table 1. The conductivity did not change appreciably in the course of the 3,600 s runs, but it did increase slightly from run to run as the proportion of NaCl increased. This could be attributed to the greater total number of ions in a NaCl solution versus a Na₂SO₄ solution of the same normality. The pH rose, probably due to the combined effects of (1) reduction of

hydronium (H⁺) ions to hydrogen gas which was stripped out of the system at the cathode and (2) the formation of a chlorine residual. The temperature fluctuated with the room temperature, dropping slightly over the course of the run, probably due to nitrogen expansion as the mixing gas bubbled through. Due to residual dye color in some of the 3,600 sec samples, direct measurement of chlorine residual was only possible for the 0.03, 0.04, and 0.05 N NaCl runs; incomplete dye removal interfered with the colorimetric endpoint for the 0.01 and 0.02 N NaCl runs. The potential stayed essentially constant, possibly decreasing slightly on average as the conductivity of the solution increased slightly. Slight decreases would not be surprising because higher conductivity results in less cell resistance, so the cell potential will decrease if current is kept constant (recall Ohm's law: potential=current×resistance).

The data for fraction of dye remaining (C_t/C_0) versus time (t) in seconds are plotted in Fig. 3. Fig. 4 is an example plot of the spectra with time for the 0.03 N NaCl run. Note that the spectra for the quenched samples are marked with an asterisk. The fraction of dye removed by excess electrochemically generated oxidant species in solution at the time of sampling (the difference between the quenched and unquenched samples) is plotted for each run in Fig. 5.

First order curves were fitted to the data for the quenched samples shown in Fig. 3; the resulting apparent first order rate constants, k , are reported in Table 2, together with the percent coefficient of variance (%COV) as a measure of variability in

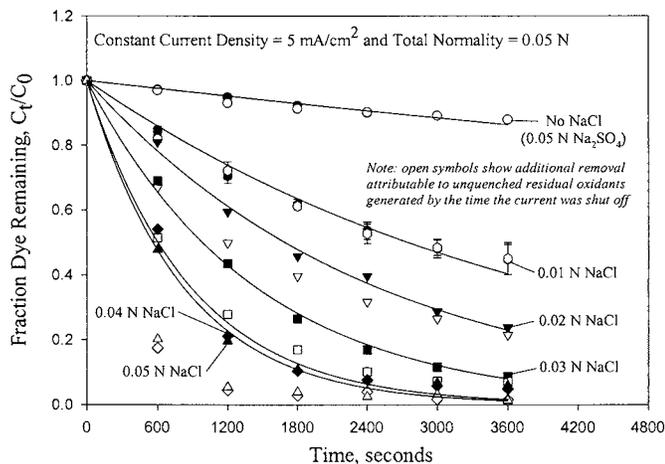


Fig. 3. Effect of chloride concentration on DR83 decolorization rate

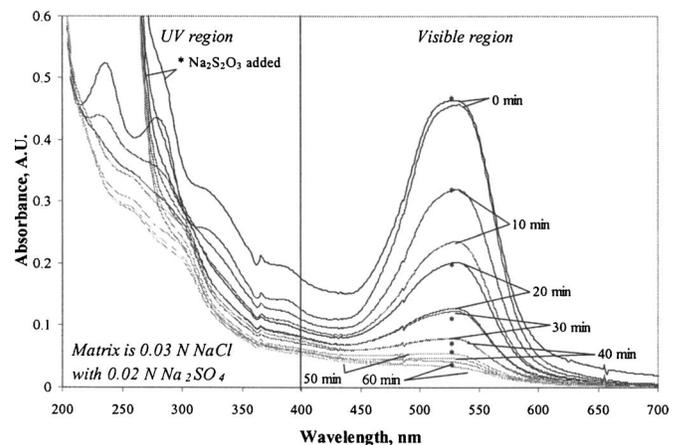


Fig. 4. Example UV-vis spectra for electrolytic treatment of DR83

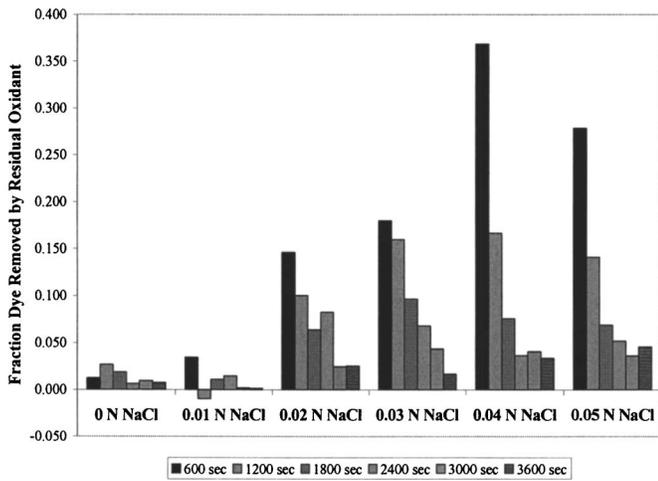


Fig. 5. Fraction of dye removed by residual oxidant as function of chloride concentration and time

each fit. The data for duplicate 0.01 N NaCl runs were averaged and the mean was plotted with error bars that represent the two values that went into the average to give a visual sense of the run-to-run variability; this was less than $\pm 10\%$ from the mean value in all cases, and usually less than $\pm 5\%$.

Discussion

There is greater than 1 order of magnitude (~ 30 times) difference in the DR83 decolorization rate constants for sulfate (0.05 N Na_2SO_4) versus chloride (0.05 N NaCl) as the anionic species. The rate for the 0.05 N Na_2SO_4 run is representative of the direct oxidation rate; the impact of indirect oxidation is readily apparent if chloride ion is present in the matrix. This is important because dye wastewater can commonly contain chloride concentrations in the 0.0003–0.3 N range, which are well within the range studied in this research. In fact, one value cited for a wastewater containing after-copperable direct dye (the same type of dye as Direct Red 83) was in the 0.015 N range (Horning 1978), and this is the range where both direct and indirect oxidation were clearly noted in our study.

The lack of difference between the fraction of DR83 remaining in both quenched and unquenched samples in the 0.01 N NaCl run implies that the oxidized chlorine species produced electrochemically at this NaCl concentration is reacting with the dye as fast as it is produced. This may be indicative of the point where chloride concentration limits the indirect oxidation rate. At higher NaCl concentrations, dye color loss continues as an un-

Table 2. Summary of Apparent First Order Rate Constants for Chloride Concentrations Studied

NaCl (N)	Na_2SO_4 (N)	Rate constant, k (s^{-1})	% COV ^a (%)
0	0.05	3.96×10^{-5}	7.27
0.01	0.04	2.51×10^{-4}	5.56
0.02	0.03	4.09×10^{-4}	3.44
0.03	0.02	7.04×10^{-4}	3.15
0.04	0.01	1.15×10^{-3}	6.28
0.05	0	1.24×10^{-3}	6.50

^aFrom curve fit.

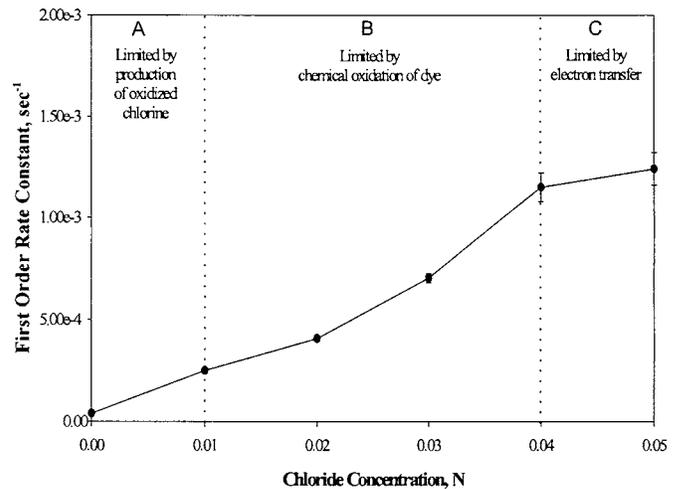


Fig. 6. First order rate constant behavior as function of chloride concentration

quenched sample sits without any direct oxidation (no current), implying that the reaction rate between the oxidized chlorine species and the dye is the rate-limiting step. This has implications for developing a treatment strategy in which the electrochemical reactor current is shut off before complete color destruction has occurred to take full advantage of indirect oxidation without creating excess chlorine residual.

The similarity of fraction of dye remaining for both quenched and unquenched samples from the 0.04 and 0.05 N NaCl runs suggests that the rate of production of oxidized chlorine species is no longer limited by the concentration of chloride at higher NaCl concentrations, but by some other factor such as electron transfer rate due to the current density. The lack of increase in free available chlorine residual for the 0.04 compared to 0.05 N NaCl runs supports this observation. The purpose of this study was to explore the impact of chloride concentration under constant operational conditions such as constant current, but these data highlight the importance of studying treatment at various current densities for a given wastewater composition when addressing reactor design.

Finally, in all the runs where an oxidant residual was formed, the biggest differences between the fraction dye remaining in the quenched and unquenched samples occurred at the earliest time points, and the values converged as time increased (Fig. 5). This implies that there may be a shift in the chlorine demand of the dye and dye metabolites related to the progress of the reaction, i.e., the demand increases with time as more fragments that react with chlorine are formed. Either that or the production of oxidized chlorine species falls off with time due to some interference on the anode surface.

It is obvious from these data that the apparent first order rate constant is a function of initial chloride concentration. One simple expression describing this relationship, in a manner similar to one proposed by Chiang et al. (1997) in their work with refractory organic pollutants, would be

$$dC_{(t)}/dt = -kC_{(t)} = -k' C_{\text{Cl}} C_{(t)} \quad (1)$$

where $C_{(t)}$ represents dye concentration at t sec., k =apparent first order rate constant determined from the data shown in Fig. 3, k' =reaction rate constant, and C_{Cl} =initial chloride concentration. If this expression is true, then a plot of k versus initial chloride concentration should yield a straight line with a slope of k' . The

relationship is not this simple, however, as the plot in Fig. 6 illustrates. Instead, the reaction kinetics seem to fall into three regions; a region in which decolorization rate is limited by the rate of production of oxidized chlorine species, a region in which decolorization rate is limited by the rate of indirect chemical oxidation of the dye, and a region in which decolorization rate is limited by the electron transfer rate, which is controlled by the current density and electrode surface phenomena.

In addition to the impact of chloride with respect to rate, there is a distinct likelihood that chlorinated organic species may be formed in the process of indirect oxidation. These compounds may be more toxic than the dyes themselves, so toxicity endpoints should be considered during process optimization. Electrolytic treatment still has the potential to continue to mineralize chlorinated organic compounds to carbon dioxide and water and the originally occurring salt via direct oxidation, if additional treatment time is allowed, and this is the subject of continuing research in our laboratory.

Conclusions

1. Electrolytic treatment of wastewaters containing DR83 takes place via direct oxidation related to current flow, as well as via indirect oxidation by reactive oxidized species formed as a result of current flow when chloride ions are present in the wastewater.
2. The rate of dye decolorization increases with increasing chloride concentration to a point where the rate of electron transfer producing oxidized chlorine species or other electrode surface phenomena becomes rate limited. In the system studied, this point was at a chloride concentration of 0.04 N NaCl (with 0.01 N Na₂SO₄ in the system to a total normality of 0.05 N).
3. The rate of indirect oxidation is slower than the rate of chlorinated oxidizing species production above a 0.01 N NaCl concentration in our system based on the increasing difference between the fraction of dye remaining in quenched versus unquenched samples.

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