Electrochemical Treatment and HPLC Analysis of Wastewater Containing Acid Dyes

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The treatment of wastewater has long been a concern of the textile industry. The industry produces large quantities of aqueous waste and dye effluent.[1] The production of a textile product involves a multitude of processes, many of which use water and a number of chemicals. This wide variety of chemicals and processes leads to wastewater which is highly variant in pollutant content. Dye effluent is highly colored and is thus an aesthetic pollutant.[1] While removal of color has been the focus of many studies on dye wastewater treatment, dye wastewater also poses a problem because of its potential carcinogenicity and toxicity.[1]

In particular, treatment technologies for carpet wastewater need more investigation. Recently, publicly owned treatment works (POTW's) in some areas of the southeastern U.S. have had difficulty meeting their discharge limits because of carpet wastewater, and thus the possibility of stronger restrictions on mill effluent is likely.[2] Carpet mills may have to install pretreatment facilities prior to discharge to a POTW. The majority of dyes present in carpet wastewater are acid dyes; therefore, this project focuses on acid dyes that could serve as models for the behavior of carpet dyes in the electrochemical treatment process.

Useful dyes are ones which will not change color and are fast to cleaning. This means that dyes in aqueous solutions do not degrade spontaneously since they are designed specifically not to degrade. Dye wastewater therefore requires treatment before disposal. Many treatment methods have been investigated and used, but no one method is successful in every case.[3] The most extensively used methods in the industry are biological systems.[4] These systems are not efficient in breaking down very stable dyes or in removing color from most dye effluent. In addition, the micro-organisms used are often killed by any heavy metals (used as mordants) which may be present in dye effluent.[4]

Andco Environmental Processes Inc. (Amherst, N.Y.) has investigated the use of electrochemical technology for wastewater treatment. The process involves the use of a sacrificial iron electrode. When a direct current is passed through the cell, $Fe(OH)_2$ is produced. It is hypothesized that the large surface area of $Fe(OH)_2$ can adsorb organic compounds and that this adsorption is the pathway for dye removal.[1,5-8] Previous studies of this electrochemical process have shown that it is an effective method for dye wastewater treatment. Researchers have found that the process removes color efficiently; color reductions of 75 to 100% have been achieved with a wide variety of dyes.[1,5-8] The process also effectively reduces organic load and toxicity. Decreases in chemical oxygen demand (COD), biological oxygen demand (BOD), total organic carbon (TOC) and toxicity to *Daphnia Magna* have been reported.[1,5-8] Dye and other dyebath constituent removal has also been established with electrochemical treatment by an aluminum electrode.[9]

Little is known about how electrochemical treatment affects color removal. Adsorption has generally been accepted as the main mechanism of dye removal by the Andco process. Weinberg investigated other possible mechanisms, such as complexation and dye degradation.[5] By using azobenzene as a model compound in the Andco electrochemical system, it was shown that identical ultraviolet absorption spectra could be measured under three circumstances—the treated solution of azobenzene, a solution of azobenzene that had been reduced by sodium hydrosulfite and a dilute solution of aniline. These results strongly suggest the reduction of the azo bond in acid dyes when the Andco system is used.

These studies with absorption spectrophotometry can be enhanced by the use of high performance liquid chromatography (HPLC) with a diode array detector, which can provide more specific information about and confirmation of the mechanism of color removal. Each species in a mixture has a characteristic retention time in a given solvent and column system. The diode array detector provides an ultraviolet/visible absorption spectrum of each component. With the use of the

ABSTRACT

Acid dye removal in aqueous solutions by electrochemical treatment was evaluated for possible use as a method for wastewater treatment. Specifically, the mechanisms by which acid dyes are removed were elucidated. The electrochemical process studied uses a sacrificial iron electrode which produces $Fe(OH)_2$ when direct current is passed through the cell. Analysis of products was performed by high performance liquid chromatography (HPLC) with a diode array detector. Because it separates all components in a mixture, HPLC allows quantitative determination of the dye in solution and monitoring of the formation of degradation products. The results of this study indicate that the mechanism for color removal by electrochemical treatment is more complex than first hypothesized; it is most likely a combination of adsorption and dye degradation. Two of the three dyes used in this study formed degradation products in solution which were not removed by further treatment. In particular, aniline was identified as one of the breakdown products formed in electrochemical treatment of C.I. Acid Red 1, implying reduction of the azo bond. Iron, in the amount of 200 mg/L, was added to 50 mg/L Acid Red 1 and produced 6.05 mg/L aniline.

KEY TERMS

Acid Dyes
Degradation
Electrochemical Treatment
HPLC Analysis
Wastewater Treatment

HPLC system for analysis of solutions treated by the Andco process, the appearance and disappearance of peaks with characteristic absorption spectra should give more information about the formation of degradation products.

The overall goal of the study reported here was to use HPLC with diode array detection to provide a better evaluation of the electrochemical treatment's effectiveness for removal of color from acid dye solutions and to begin to understand the mechanism by which color is removed. The main objectives of the study were to refine existing HPLC methods for the analysis of acid dye solutions before and after treatment, to use HPLC to monitor color removal in electrochemically-treated acid dye solutions of varying concentration and to characterize any major degradation products which remain in solution after the electrochemical treatment.

Experimental

Reagents

The dyes used in this study were C.I. Acid Red 1, C.I. Acid Blue 127 and C.I. Acid Red 183. All were obtained in "as sold" powdered form. The structures of the three dyes are shown in Fig. 1. Laboratory grade NaCl and a 0.2% solution of the anionic acrylamide coagulant polymer, Andco 2600 were used in the electrochemical treatments. Reagent grade HCl and analytical grade NaOH were used for pH adjustment in the electrochemical treatments. In the HPLC analyses, HPLC grade methanol and a 1M aqueous solution of the ion-pairing reagent, tetrabutylammonium dihydrogen phosphate were used. Aqueous solutions were made with ultra-pure water prepared using deionized water passed through a Barnstead NANOpure II 4-Module System and subsequently distilled in a Corning MEGAPURE Model MP-1 Still. Reagent grade aniline was used for the quantitative determination of aniline in Acid Red 1 solutions.

All solutions were prepared using the chemicals described above. For each group of electrochemical experiments, a dye stock solution of approximately 1000 mg/L in ultra-pure water was made. For each HPLC analysis, four analytical calibration standards of the given dye were prepared at concentrations spanning the expected concentration ranges of the treated samples.

Electrochemical Treatments

Solutions of each of three dyes, Acid Red 1, Acid Blue 127 and Acid Red 183, were treated with the Andco laboratory scale iron electrode (L-cell). The L-cell is made up of three plates of cold-rolled carbon steel separated by a gap of 1/8-inch. The reactions which take place when current is passed through the electrodes may be summarized as follows:

Anode (Oxidation)

$$Fe \text{ ----> } Fe^{2+} + 2e^- \quad \text{Eq. 1}$$

Cathode (Reduction)

$$2\,H_2O + 2e^- \text{----> } H_2 + 2OH^- \quad \text{Eq. 2}$$

Overall

$$Fe + 2H_2O \text{ ----> } Fe(OH)_2 + H_2 \quad \text{Eq. 3}$$

The amount of iron addition to a given solution is determined by the amount of time that current is allowed to flow through the cell. A schematic diagram of the electrochemical process is shown in Fig. 2.

Solutions of 0, 15, 25 and 50 mg/L concentration of each of the three dyes were prepared by diluting an aliquot

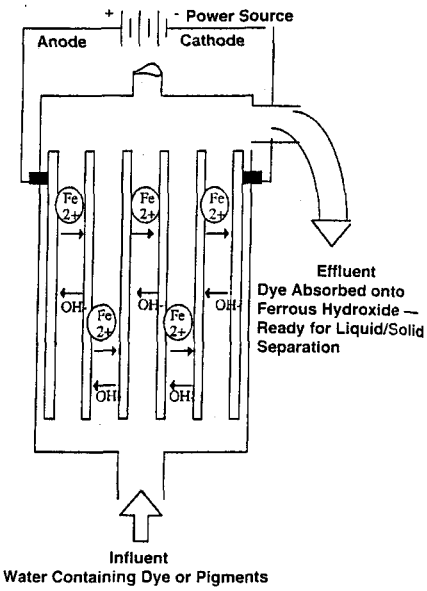

Fig. 2. Schematic of electrochemical process.

of the 1000 mg/L stock solution. 400 mL of solution were placed in a 600 mL beaker for treatment. To provide a conductive environment for the L-cell, 0.4 g of NaCl were added to each solution, since solutions were made with deionized, distilled water. Preliminary experiments with acid dyes in the electrochemical system indicated that the process does not remove dyes efficiently unless salt is added. The formation of iron hydroxide sludge and the increase in pH during electrochemical treatment supports the hypothesis that the dominant half reactions are the ones shown in Eqs. 1-3, rather than ones involving chloride.

Five solutions of each concentration were treated with the L-cell. A different amount of iron was added to each solution. The amount of iron added ranged from 0 mg/L to that required for

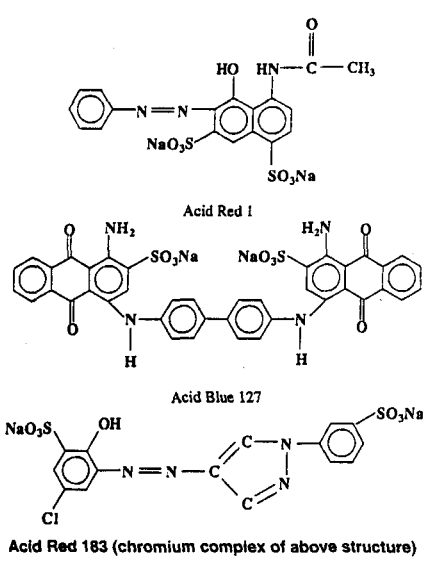

Fig. 1. Structures of dyes studied.

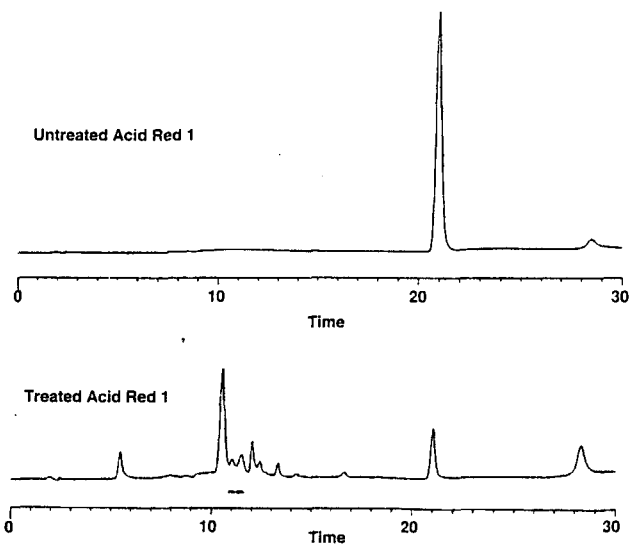

Fig. 3. Typical chromatograms of 50 mg/L Acid Red 1 solutions, untreated (505 nm) and treated with 100 mg/L iron (253 nm).

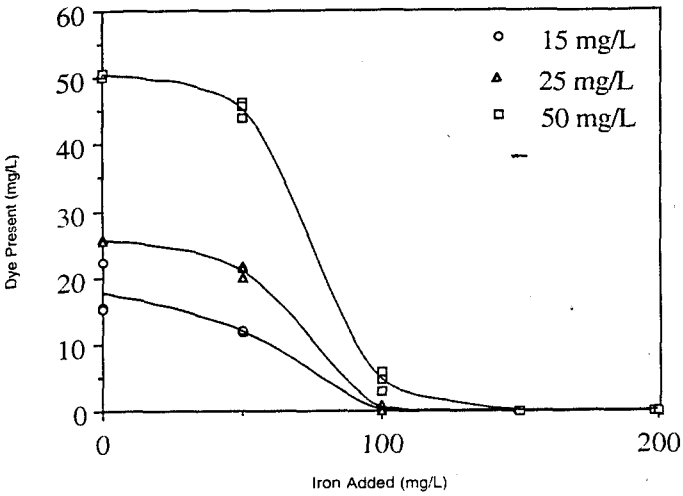

Fig. 4. Acid Red 1 dye remaining after electrochemical treatment as a function of iron addition; initial concentrations of dye: 15, 25, 50 mg/L.

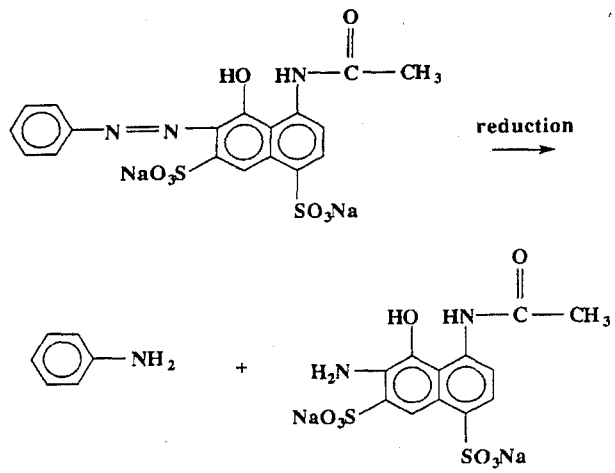

Fig. 5. Reduction of azo linkage in Acid Red 1.

maximum dye removal, based on preliminary experiments for each dye. For Acid Red 1, the iron addition levels were 0, 50, 100, 150 and 200 mg/L. For Acid Red 183 and Acid Blue 127, the iron addition levels were 0, 25, 50, 75 and 100 mg/L. Following electrochemical treatment, the solutions were stirred for five minutes to vent hydrogen gas. After degassing, the pH was adjusted to 8.3 to 8.9 with 0.01M HCl and 0.01M NaOH.

Following pH adjustment, 1.0 mL of Andco 2600 flocculent polymer was added to the solution. The solution was allowed to flocculate and was then filtered through a glass microfiber filter. The filtrate was collected for HPLC analysis. Each of these batches (four concentrations × five iron addition levels = 20 samples) were repeated three times.

HPLC Methods

The quantity of dye present in solution after electrochemical treatment was determined by high performance liquid chromatography (HPLC) using a Hewlett Packard 1090A liquid chromatograph with a Rheodyne 7010 injection valve and a 200 mL sample loop. The column used was a 4.6 mm I.D. × 15 cm Supelcosil LC-8-DB column with 3 µm particle size; the guard column was a 2 cm Supelguard LC-8-DB.

An HPLC method was developed for each dye by adapting a method from the literature.[10] The mobile phase used was 0.005M tetrabutylammonium phosphate (TBAP) in methanol/water at a flow rate of 1.0 mL/min. The ratios of methanol:water depended on the dye being analyzed (60:40 for Acid Red 1 and Acid Red 183 and 80:20 for Acid Blue 127). Retention times were approximately 3.7 minutes for Acid Red 1, 4.7 minutes for Acid Blue 127 and 4.0 minutes for Acid Red 183. The diode array detector was set to monitor absorbance at the wavelengths of maximum absorption for a given dye. Multiple wavelengths were monitored for each dye: 253, 505 and 535 nm for Acid Red 1; 253 and 590 nm for Acid Blue 127; and 257, 321, 357 and 492 for Acid Red 183. The wavelengths chosen for integration and calibration of the parent dye were 505 nm for Acid Red 1, 253 nm for Acid Blue 127 and 257 nm for Acid Red 183.

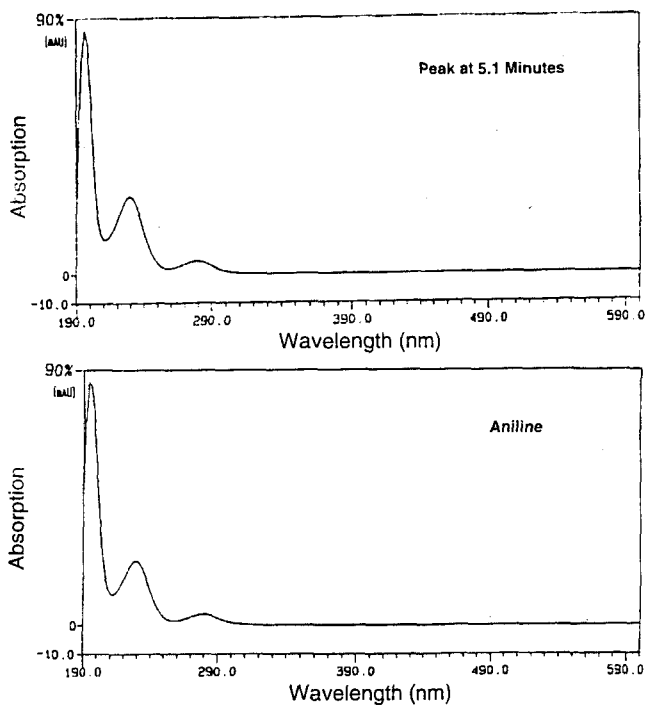

Fig. 6. Comparison of UV/Visible spectra of degradation product (5.1 minute) from Acid Red 1 and aniline.

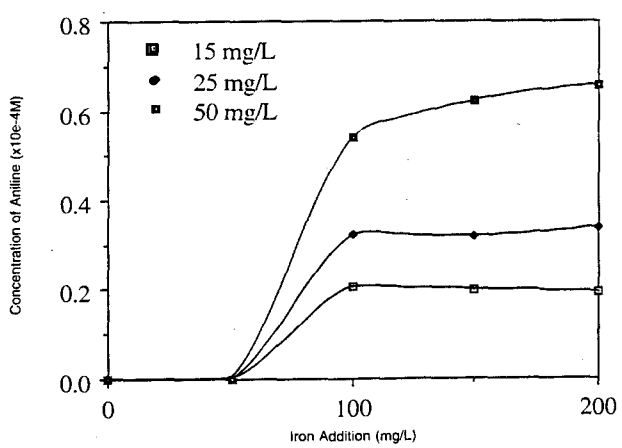

Fig. 7. Aniline (proposed) concentration as a function of iron addition in treated Acid Red 1; initial concentrations of dye: 15, 25, 50 mg/L.

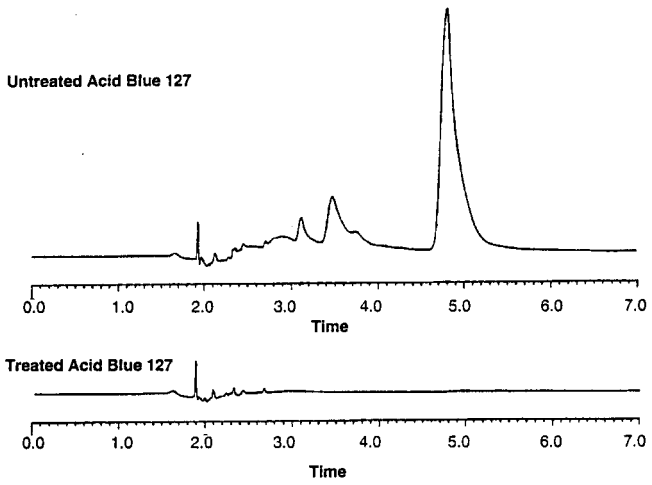

Fig. 8. Typical chromatograms of 50 mg/L Acid Blue 127 solutions, untreated and treated with 100 mg/L iron (253 nm).

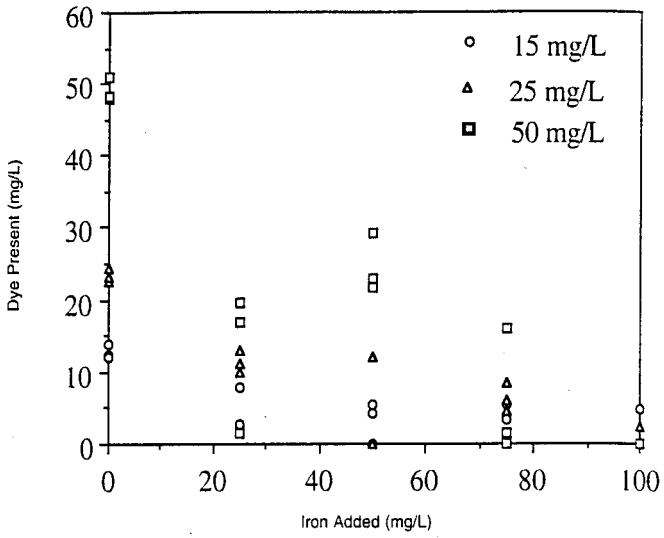

Fig. 9. Acid Blue 127 remaining after electrochemical treatment as a function of iron addition; initial concentrations of dye: 15, 25, 50 mg/L.

Chromatograms of some treated samples (monitored at two of the wavelengths, 253 nm for Acid Red 1 and 257 nm for Acid Red 183) showed peaks that were not present in chromatograms of untreated samples. These peaks were assumed to be degradation products, and HPLC methods were developed to separate them effectively from each other and the dyes. Peaks were noted on the 253 nm monitored chromatogram for treated Acid Red 1. To achieve satisfactory separation of the breakdown products from the parent compound, the following gradient elution was used. The first part of the gradient was from 35:65 to 50:50 methanol:water in six minutes. Over this period of six minutes, the flow rate was decreased from 1.0 mL/min. to 0.75 mL/min. These conditions (0.75 mL/min. and 50:50) were then held for 10 minutes. Following this, a second set of conditions were run, using a gradient from 50:50 to 60:40 methanol: water in four minutes.

Peaks were noted on the 257 nm monitored chromatogram for treated Acid Red 183. To achieve separation of the breakdown products from the parent compound, the following gradient elution was used. The gradient went from 50:50 to 60:40 methanol: water in four minutes. The mobile phase was then held at 60:40 methanol: water until all compounds were eluted (approximately six minutes).

Results and Discussion

Acid Red 1

Typical chromatograms of 50 mg/L solutions of untreated (monitored at 505 nm) and treated (with 100 mg/L iron, monitored at 253 nm) Acid Red 1 are shown in Fig. 3. The treated dye chromatogram shows a number of breakdown products. The retention time for Acid Red 1 in these separations was 20.8 minutes, and the major breakdown products had retention times of 5.1, 10.5 and 12.0 minutes. The peak at 10.5 minutes had the greatest area, but without standards to calibrate, relative concentrations could not be determined.

The area of the 20.8-minute peak was plotted against iron addition for all treatments of Acid Red 1. The results are shown in Fig. 4. One hundred percent removal was achieved for all concentrations of dye at 150 mg/L iron addition. At low levels of iron addition, very little dye is removed (as followed quantitatively by the area of the parent dye peak monitored at 505 nm) and no breakdown products appear in the chromatograms. At higher levels of iron addition, dye removal is much greater and breakdown products appear in the chromatograms. It seems that at low levels of iron addition, dye removal is solely by adsorption. At higher levels of iron addition, the dye removal mechanism is a combination of adsorption and degradation.

It is known that the azo linkage in dyes such as Acid Red 1 is highly susceptible to reduction.[11] It is therefore possible that the breakdown products present in the chromatograms are the result of a reduction reaction induced by the electrochemical treatment process. This hypothesized reduction is shown in Fig. 5, and one of the products is aniline.[5] A sample of aniline was analyzed using the HPLC separation method developed for Acid Red 1 and its breakdown products; i.e., by monitoring at 253 nm. The retention time of aniline is 5.1 minutes, which corresponds exactly to the retention time of one of the major breakdown products observed in the chromatograms of treated solutions. The diode array detector was used to take an ultraviolet/visible spectrum of aniline and the breakdown product at 5.1 minutes. The two spectra are shown in Fig. 6. Since the spectra are identical, the breakdown product was assumed to be aniline.

Concentrations of aniline in solutions of treated Acid Red 1 were calculated from the area of the 5.1 minute peak monitored at 253 nm and plotted as a function of iron addition. The results are shown in Fig. 7. 200 mg/L of iron addition to 50 mg/L Acid Red 1 produced 6.05 mg/L of aniline. This may be a cause for concern since the suggested ambient limit of aniline in water is 0.26 mg/L, and it does not appear to be removed by electrochemical treatment.[12] It has been shown, however, that aniline is readily oxidized by biological treatment, so it may not pose a toxicity problem if the effluent is treated at a POTW.[5]

The ultraviolet/visible spectra of the other two major breakdown products of Acid Red 1 were not as revealing as the spectrum for the breakdown product at 5.1 minutes. Examination of the spectra indicates that the structures of the breakdown products are less conjugated than the structure of the dye since the spectra show no absorption in the visible region. The reductive cleavage of the azo bond in Acid Red 1 would produce a substituted naphthalene, in addition to aniline. When the spectra of the peaks at 10.5 and 12.0 minutes are compared to the spectrum of naphthalene, it appears likely that the two breakdown products are substituted naphthalenes. Determination of the exact functional groups is not

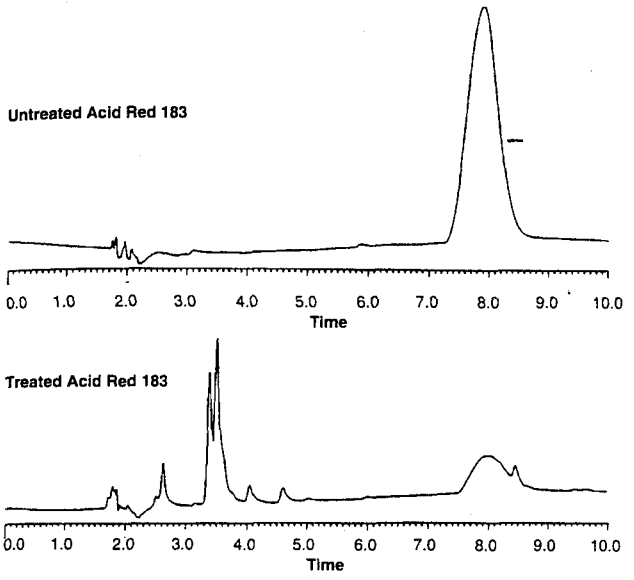

Fig. 10. Typical chromatograms of 50 mg/L Acid Red 183 solutions, untreated and treated with 100 mg/L iron (257 nm).

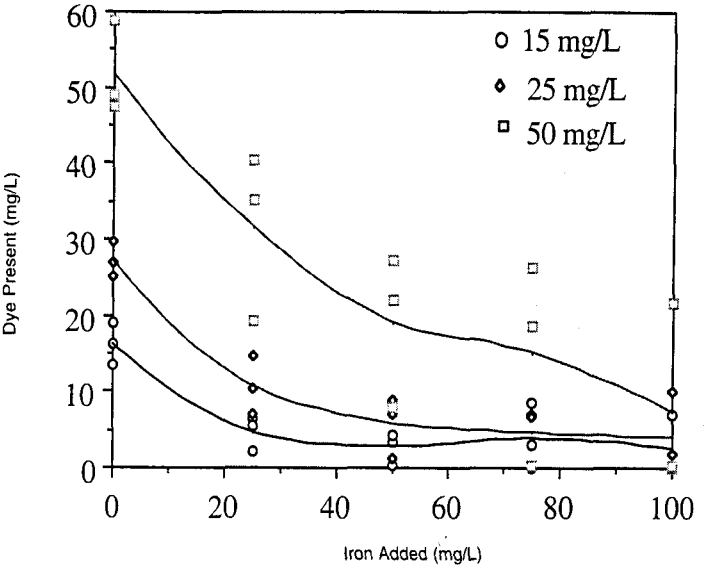

Fig. 11. Acid Red 183 remaining after electrochemical treatment as a function of iron addition; initial concentrations of dye: 15, 25, 50 mg/L.

possible from an ultraviolet/visible spectrum. When the area under the peaks at 10.5 and 12.0 minutes are plotted against iron addition (not shown), it appears that these breakdown products are removed by electrochemical treatment.

Acid Blue 127

Typical chromatograms of 50 mg/L solutions of untreated and treated (with 100 mg/L iron) Acid Blue 127 are shown in Fig. 8. The chromatogram of untreated Acid Blue 127, monitored at 253 nm, shows one major peak at 4.8 minutes and a number of smaller peaks between three and four minutes, assumed to be impurities, as well as some noise below three minutes. The chromatogram of treated Acid Blue 127, monitored at 253 nm, shows none of these peaks, only noise, indicating complete removal of the dye and its impurities from solution.

Areas of the 4.8 minute parent dye peak in all treatments of Acid Blue 127 were plotted against iron addition, and the results are shown in Fig. 9. One hundred percent color removal was achieved on most (seven out of nine) samples with 100 mg/L iron addition. The data for this dye are extremely scattered; this could be due to competition between the dye and its impurities or breakdown products for adsorption onto the $Fe(OH)_2$.

It does not appear that any breakdown products are formed in the treatment of Acid Blue 127 since no additional peaks appear in chromatograms of treated solutions. This is not surprising since the anthraquinone structure of Acid Blue 127 is much less susceptible to oxidation and reduction than the azo structures of the two red dyes. Removal of Acid Blue 127 therefore appears to be solely by adsorption. If breakdown products are formed, they are removed by the electrochemical process. Examination of the chromatograms indicates that the impurity concentration, as a function of iron addition, follows the same trend as the dye concentration.

Acid Red 183

Typical chromatograms of 50 mg/L solutions of untreated and treated (with 100 mg/L iron) solutions of Acid Red 183, monitored at 257 nm are shown in Fig. 10. The retention time for the parent peak of Acid Red 183 is 7.8 minutes. The chromatogram of treated Acid Red 183 shows a number of breakdown products. The major degradation products had retention times of 3.4 and 3.5 minutes.

The results of all treatments of Acid Red 183 solutions, as followed quantitatively by the area of the 7.8 minute peak monitored at 257 nm are shown in Fig. 11. One hundred percent color removal was achieved on three of the nine samples treated with 100 mg/L iron and two of the nine samples treated with 75 mg/L iron. The data for this dye are extremely scattered so it is difficult to make generalizations about the treatment's effectiveness. One possible explanation for the scatter in this data is that since Acid Red 183 is a chromium complex azo dye, some complexation may be taking place during the electrochemical treatments.

The ultraviolet/visible spectra of the major breakdown products give little information about their structures. The structures of the breakdown products are less conjugated than that of the original dye since no absorption in the visible region is observed in their spectra. The spectra of the two breakdown products are almost identical, which suggests that they are isomers of the same compound. This is also supported by the fact that their retention times are very similar. When the area under the peaks at 3.4 and 3.5 minutes are plotted against iron addition (Fig. 12 and Fig. 13), it appears that these breakdown products are not removed by electrochemical treatment.

Conclusions

Electrochemical treatment experiments show that the Andco iron electrode can be very effective in color removal from acid dye solutions. For solutions in the 15 to 50 mg/L range, 100% color removal was affected by 150 mg/L iron addition to solutions of Acid Red 1, by 100 mg/L iron addition to most solutions of Acid Blue 127 and by 75 to 100 mg/L iron addition to some solutions of Acid Red 183.

The use of HPLC for analysis of treated solutions proved to be superior to spectrophotometry. Because HPLC affects separation of the dye from any other compounds in the treatment bath, quantitative analysis of dye removal is possible. Obtaining good quantitative data with spectrophotometry was not possible, since other compounds present in the treatment bath interfered with spectral measurements.

In addition to quantitative analysis, HPLC provides qualitative information

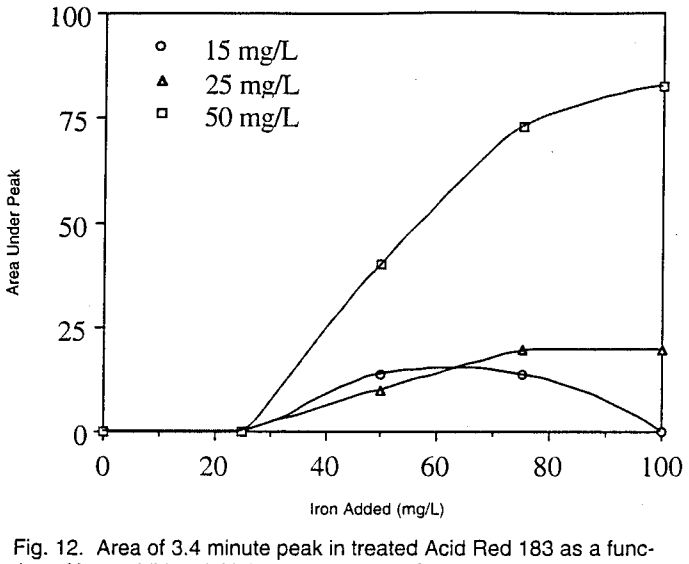

Fig. 12. Area of 3.4 minute peak in treated Acid Red 183 as a function of iron addition; initial concentrations of dye: 15, 25, 50 mg/L.

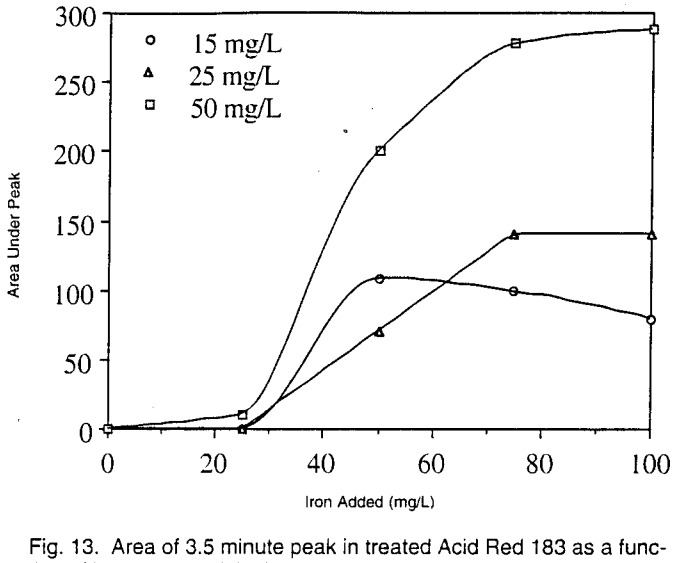

Fig. 13. Area of 3.5 minute peak in treated Acid Red 183 as a function of iron addition; initial concentrations of dye: 15, 25, 50 mg/L.

about the formation of breakdown products in the electrochemical process. Chromatograms of treated Acid Red 1 and Acid Red 183 show peaks which were not present in chromatograms of the untreated dye. The presence of these peaks indicates that dye breakdown is occurring in the electrochemical process. Chromatograms of treated Acid Blue 127 show no peaks, suggesting that no degradation products absorbing at any of the wavelengths monitored remain in solution. Color removal of Acid Blue 127 could be due to simple adsorption, or if degradation occurs, degradation products could also be adsorbed.

Characterization of the breakdown products found in chromatograms was attempted. The ultraviolet spectrum of the peak at 5.1 minutes in chromatograms of treated Acid Red 1 suggests that the product might be aniline. This suggestion was partly confirmed by analysis of an aniline sample which had an identical retention time and ultraviolet spectrum. The other ultraviolet data suggest that breakdown products formed by reduction of the azo bond are present in treated solutions of Acid Red 1. The ultraviolet data for the breakdown products of Acid Red 183 are inconclusive. Future work should include mass spectrophotometry of these breakdown products to confirm the hypotheses from the ultraviolet data and to deduce the exact structures of the products.

Acknowledgments

The authors would like to thank Andco Environmental Processes for providing laboratory scale electrodes, and Crompton & Knowles Corp., Aakash Chemicals & Dyestuffs, Inc. and Sandoz Chemicals for providing the dyes used in the experiments. Funding for this project was provided by a grant from the Special Projects Fund of the New York State College of Human Ecology.

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