

CHARACTERIZATION OF A REACTIVE DYE,
CIBACRON VIOLET P-2R, DURING AN
ELECTROCHEMICAL OXIDATION PROCESS

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ABSTRACT

The aim of this study was to characterize the chemical changes in textile industrial wastewater containing dyes when electrochemical treatment is introduced. This study concentrated on one reactive dye, Cibacron Violet P-2R, and the changes that take place in each step of the electrochemical treatment process. Improvements for the electrochemical bulk oxidation conditions are also introduced to achieve the best possible results.

The work was commissioned by the Universitat Polytechnica de Catalunya in Terrassa. The project consisted of experimental working amidst the reactive dye selected of modifying the results to a more understandable form and of an analysis of the results.

The characterization of the dye was accomplished with infrared spectroscopy (FTIR) and UV-Vis spectroscopy. The electrochemical behaviour of the dye was studied using an electrochemical technique called cyclic voltammetry. Electrochemical bulk oxidation of the dye was performed to achieve the required results. The oxidation products were analysed with FTIR and UV-Vis spectroscopy.

The results showed that many changes take place in the chemical structure of the dye during the electrochemical oxidation process. Changes can also be seen before oxidation itself occurs. There are also changes in other parameters due to electrochemical oxidation, for example, in conductivity.

Electrochemical oxidation is a functional way to treat textile industrial wastewaters but further research is required to obtain more reliability to the results achieved by this study.

Keywords: reactive dye, electrochemical oxidation, characterization, spectra

Lahden ammattikorkeakoulu
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TIIVISTELMÄ

Tässä työssä keskitytään tunnistamaan väriaineessa tapahtuvat kemialliset muutokset, kun tekstiiliteollisuuden jätevesiä käsitellään elektrokemiallisin menetelmin. Reaktiivinen väriaine, jonka kemiallisia muutoksia seurattiin, on nimeltään Cibacron Violet P-2R. Työn tarkoituksena oli seurata, millaisia muutoksia väriaineen kemiallisessa rakenteessa tapahtuu elektrokemiallisen hapetuksen eri vaiheissa. Työssä on esitetty kehitysehdotuksia tekstiiliteollisuuden jäteveden elektrokemialliseen hapetukseen.

Työssä väriaineen tunnistus tapahtui käyttämällä kahta tunnistusmenetelmää: Infra-puna spektroskopiaa (FTIR) ja UV-Vis spektrometriaa. Väriainetta hapetettiin elektrokemiallisesti käyttämällä apuna syklistä voltmetria. Elektrokemialliset hapetus-tuotteet, joita menetelmässä syntyi, analysoitiin käyttämällä FTIR ja UV-Vis spektrometria. Työn tarkoituksena on myös optimoida elektrokemiallisen hapetuksen olosuhteet siten, että häiriötekijöitä ei esiinny tuloksissa.

Tulokset osoittivat, että väriaineen kemiallisessa rakenteessa tapahtui monia muutoksia elektrokemiallisen hapetuksen aikana. Elektrokemiallinen hapetus vaikuttaa myös muihin olosuhteisiin (esim. sähkönjohtokyky) ja tämä on hyvä huomioida lisätutkimuksia tehdessä.

Laboratoriomittakaavassa saatujen tulosten perusteella menetelmä soveltuu valitun väriaineen käsittelyyn jätevedessä, mutta tarkemmat tutkimukset ovat tarpeen, jotta olisi mahdollista saada tarkempia tuloksia väriaineen kemiallisessa rakenteessa tapahtuneista muutoksista.

Avainsanat: reaktiivinen väriaine, elektrokemiallinen hapetus, kemiallinen rakenne

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1 INTRODUCTION

These days the production of coloured textiles is one of the basic technologies. Textile consumption is steadily increasing in many countries, primarily in Asia, but also worldwide due to the growth of world population. This has led to a situation where coloured textiles are produced on a large industrial scale. Before textiles were mainly dyed with plant dyes and the use of animal dyes was restricted only to special cases. Today, plant dyes have more or less been left aside and synthetic dyes have taken their place. (Leube 2003, 339-340).

In textile industry the high water consumption makes it important to study the reuse of wastewaters. Many different treatments have been studied to make textile wastewaters reusable. (Bes-Piá, Mendoza-Roca, Alcaina-Miranda, A. Iborra-Clar, M.I. Iborra-Clar 2002). Textile industrial wastewaters can be treated with various techniques. Available technologies are, for example, biological treatment, chemical precipitation, ultra filtration, carbon adsorption, and oxidation with ozone. The main problems with these techniques lie in the lacking efficiency of pollutant reduction and the cost of treatment for the large amount of wastewaters. (Demmin & Andco 1988).

The use of electrochemical techniques for the treatment of industrial effluents and process streams is rapidly increasing (Scott 1995, 119). Traditionally, wastewaters from textile industry are treated biologically, physically or chemically. Various combinations of these techniques are also applied. By means of electrochemical oxidation, pollutants in wastewaters can be mineralised. (Xuejun, Zhemin, Xiaolong, Yaobo&Wenhua 2005)

In this study, a reactive azo dye, Violet Cibacron, was studied to gain information on the changes in the chemical structure after electrochemical oxidation. The objective of this study was to identify the chemical groups that react in electrochemical oxidation and to optimize the conditions during oxidation. The experimental part took eight

weeks and during that time different methods were introduced to characterize textile industrial wastewater. The experimental part of the study was accomplished in the research laboratory of Universitat Polytechnica de Catalunya (UPC).

2 DYES AND OTHER CHEMICALS IN THIS STUDY

2.1 Reactive dyes

Reactive dyes were discovered in 1954. After this research into reactive dyes became intensive and it still continues today. According to Hunger world textile production has grown steadily. Dye manufacturers have concentrated on producing dyes for the two most important textile fibres: cotton and polyester. The geographical focus of dye production lies in Germany, England and Switzerland. (Hunger 2003, 1-2).

Reactive dyes can be classified in five chemical groups: azo (including metallized azo), triphendioxazine, phthalocyanine, formazan and anthraquinone. Reactive dyes form a covalent bond with the fiber. The existence of the covalent bond makes it possible to gain excessively high washfastness properties by rather simple dyeing methods. (Hunger 2003, 3). According to Hunger (2003, 3) "A marked advantage of reactive dyes over direct dyes is that their chemical structures are much simpler, their absorption spectra show narrower absorption bands, and the dyeings are brighter."

2.2 Azo dyes

The azo dyes account for over 50% of all commercial dyes and the dyes in this class have been studied more than any other class. Azo dyes contain usually one to three azo groups (-N=N-). Four or more azo groups can also be found but more rarely. Gregory and Hunger (2003) describe the structure of azo groups in the following way: "Azo group is attached to two groups, of which at least one, but more usually both, are aromatic." Usually the most reactive dyes are in the class of azo dyes. (Hunger 2003, 14)

Apart from the textile industry azo dyes are also used as chromophores in diffusion-transfer imaging systems. Photography industry utilizes azo dyes in many other ways. For example, azo dyes apply in colour masking and in silver dye bleach process. (Filosa 2003, 519-520)

2.3 Other chemicals

To study the textile industrial wastewaters many chemicals are needed. For infrared spectroscopy potassium bromide is often applied. Bases and acids are generally the two most important substances to adjust the pH. Sodium hydroxide (NaOH) is one of the most commonly used bases.

Potassium bromide (KBr) is a salt. It is colourless to white solid that is odourless. It is soluble in water and neutral in solution. (Material safety data sheet 2003). These days potassium bromide is used as a laboratory reagent and a veterinary drug. For dogs and cats it is used to control epilepsy and seizures. (Foster & Smith 2007). Potassium bromide is used as a sedative in cattle and other animals. Previously potassium bro-

mide was applied as a sedative also in humans. (The European Agency for the Evaluation of Medicinal Products 1999).

Sodium hydroxide (NaOH) is an odourless manufactured substance. At room temperature, sodium hydroxide is a white crystalline solid that is very corrosive. In general, it is in solid form when it absorbs moisture from the air. (Agency for Toxic Substances and Disease Registry 2007). Sodium hydroxide may produce heat when diluted with water or when in contact with moisture. It is a strong base and that may be hazardous to the environment. (International Occupational Safety and Health Information Centre (CIS) 2007).

Dimethylformamide (DMF) is colourless to yellow liquid. It produces toxic fumes when heated. (International Occupational Safety and Health Information Centre (CIS) 2004). Dimethylformamide has a production volume over 1 million pounds per year in the U.S. and this makes the chemical a high production volume chemical (Scorecard 2005). Dimethylformamide is used as an industrial solvent in utilizing to process polymer fibres among other things. Therefore, the exposure to this chemical usually occurs at work. (Environmental Protection Agency 2007).

3 METHODS FOR WASTEWATER ANALYSIS IN THIS STUDY

3.1 Ultraviolet-visible spectrophotometer

An ultraviolet-visible spectrophotometer (UV-Vis) is a device which analyzes on which degree a given sample absorbs different spectra of light. The device functions in the visible and ultraviolet wavelengths. A more simple way to express the function of UV-Vis spectrophotometer is to state that it analyses the colour of the sample. (Everything 2, 2005). Wikipedia (2007) clarifies the function of the device in the fol-

lowing way: “It measures the intensity of light passing through a sample, and compares it to the intensity of light before it passes through the sample. Samples for UV/Vis spectrophotometer are most often liquids, although the absorbance of gases and even of solids can also be measured.”

3.2 Fourier Transform Infrared

“Fourier Transform Infrared Spectroscopy (FTIR) is an analytical technique used to identify organic materials. This technique measures the absorption of various infrared light wavelengths by the material of interest. These infrared absorption bands identify specific molecular components and structures.” (Materials Evaluation and Engineering, 2000). The measurement occurs when infrared passes through the sample and is detected after this. The FTIR is a single beam spectrometer and therefore does not measure the background automatically. It must therefore be measured separately before analysing the sample. (Eaton, 2007).

3.3 Electrochemical techniques and Cyclic Voltammetry

It has been shown that with electrochemical technology textile industrial wastewaters can be treated effectively and economically. In the beginning electrochemical technology was developed for removing hexavalent and other heavy metals from wastewaters. Shortly after this technology was developed it became clear that electrochemical treatment reduced colour, BOD (biochemical oxygen demand) and COD (chemical oxygen demand) very efficiently. (Demmin & Andco 1988).

Electrochemical reactions take place in an electrolytic cell and the reactions involve the flow of electrons through a conductor (Fine&Beall 1990, 749). The electrochemi-

cal reaction often involves two separate reactions that can take place simultaneously. These processes are initiated by the transfer of charge. To gain reactions electrodes must be placed in conducting liquids or salts. At a cathodic surface, the process involves the reduction of species by the impact of electrons whereas the other process involves the oxidation of species at an anodic surface. (Scott 1991, 4).

According to the education material of New Mexico state university:

“Cyclic voltammetry is the most widely used technique for acquiring qualitative information about electrochemical reactions. The power of cyclic voltammetry results from its ability to rapidly provide considerable information on the thermodynamics of redox processes and the kinetics of heterogeneous electron-transfer reactions, and on coupled chemical reactions or adsorption processes. Cyclic voltammetry consists of scanning linearly the potential of a stationary working electrode, using a triangular potential waveform. Depending on the information sought, single or multiple cycles can be used. During the potential sweep, the potentiostat measures the current resulting from the applied potential. The resulting plot of current vs. potential is termed a cyclic voltammogram. The cyclic voltammogram is a complicated, time-dependent function of a large number of physical and chemical parameters.”

(New Mexico state university, 2007).

The possibility to observe the reduction wave and the oxidation wave simultaneously is useful when studying the electrode processes. From the cyclic voltammograms, electrode kinetic and electrosorption processes can be studied in detail. (Installation and Diagnostics Guide for Autolab with PGSTAT30, 2000).

4 EXPERIMENTS

4.1 Experimental initial conditions

The study was conducted in a research laboratory of UPC, Terrassa. The reactive dye, Violet Cibacron, was studied in water solutions and in two other solvents: ethanol and dimethylformamide (DMF). The chemical structure of the dye can be seen from Figure 1.

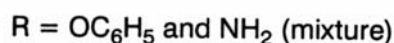
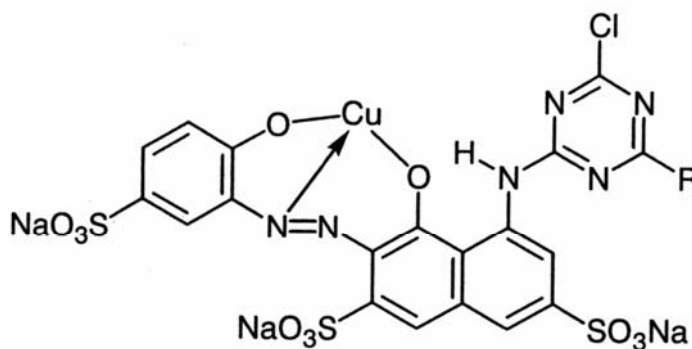


FIGURE 1. The chemical structure of Violet Cibacron

In order to achieve the same initial condition as those in the wastewater treatment plant, pre-treatments had to be accomplished (Figure 4.). In the beginning, a water diluted dye solution was prepared. The concentration of this solution (mother solution) was set to 0,2 g/l. From this mother solution the final solution to be analyzed was prepared. In the final solution the concentration of the dye was adjusted to the level of 0,1g/l and pH was adjusted to 12 by using sodium hydroxide. After this hydrolyzation took place for one hour. Figure 2 presents how hydrolysed dye solution of

violet cibacron appears. Finally, after hydralization pH and conductivity were adjusted to the levels wanted in this study. pH was adjusted to 9 by introducing sulphuric acid, H_2SO_4 , (96%) and conductivity was set to 20 000 $\mu\text{S}/\text{cm}$ with sodium sulphate anhydrous (Na_2SO_4). After hydralization, pH and conductivity adjustments, the dye solution could be oxidized electrochemically.

The conductivity of the blank solution prepared from water was adjusted to the same level than with dye solution diluted in water. The pH in water diluted blank solution was not adjusted in the same level with the dye solution. With other solvents used in this study, DMF and ethanol, conductivity was raised into the highest level possible.



FIGURE 2. The hydrolysed dye solution of violet cibacron.

4.2 Measurements

4.2.1 UV-Vis

In the beginning, the wave length where maximum absorbance appears with the dye was studied. Afterwards, a calibration line was created to see the dependency between absorbance and concentration (APPENDIX 1). The Calibration line was created by using these absorbance levels obtained from the previous tests (APPENDIX 2). Absorbance from 190 to 900 nm was measured with UV-VIS recording spectrophotometer UV-2401 PC.

Concentration of the original dye solution (concentration 0,1 g/l) was pursued for 12 days to presage if any changes occur spontaneously. In order to confirm that the initial concentration has not changed during different treatments, ultraviolet spectrometer was applied in each stage of the process:

- 1) Dye solution with pH 12 and concentration 0,1 g/l.
- 2) Dye solution after hydralization
- 3) Dye solution after pH and conductivity adjustment
- 4) Dye solution after electrochemical oxidation

4.2.2 FTIR

To characterize the changes in chemical structure of the dye, infrared spectrometer was used during the process. Infrared spectra were collected four times (Figure 4). In this study spectrometer Avatar System 320 was applied in order to gain the infrared spectra. As a detector there was DTGS KBr. Mirror velocity of the spectrometer was 0.6329. For every sample infrared spectrum was collected between 4000 and 500 cm^{-1} .

To be able to measure absorbance with infrared spectrometer from liquid sample it is essential to evaporate this liquid. In each evaporation 50ml of the dye solution was consumed to gain enough powder for FTIR. After evaporation this powder mixed with potassium bromide could be used to create a tablet. The device used to prepare the tablets is shown in Figure 3.



FIGURE 3. Device to prepare tablets for infrared spectra analyses.

Absorbance for each tablet was measured twice: right after preparing the tablet and after retaining it in the oven for 24 hours. The temperature in the oven was 60 degrees. The purpose of keeping the tablets in the oven for 24 hours was to remove moisture.

The components of interest in this study are: $-\text{SO}_3\text{Na}$, $\text{N}=\text{N}$, $\text{N}-\text{H}$, $-\text{NH}_2$, 1,3,5-triazine, benzene, naphthalene, 1-oxygenbenzene, 1-nitrogenbenzene and 1-chlorinetriazine.

The stages in which different parameters were tested (with FTIR and UV-Vis) can be seen in Figure 4.

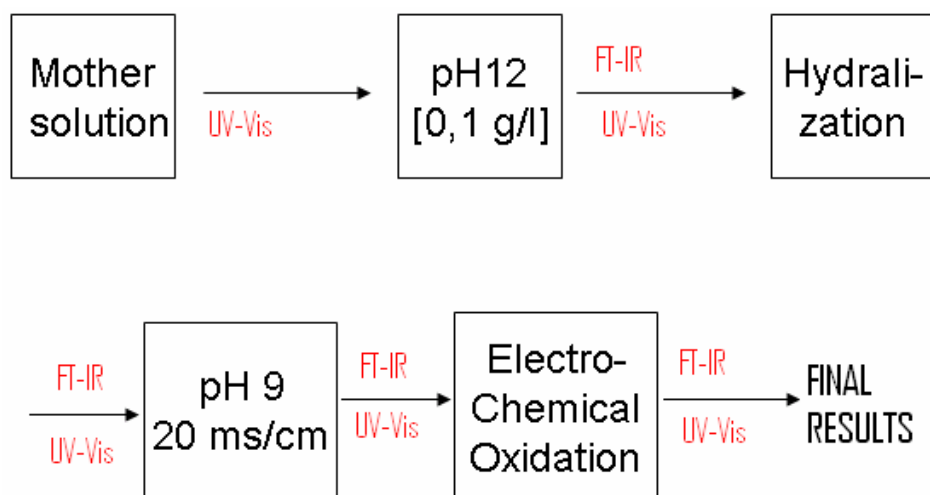


FIGURE 4. The analyses during experimental working

4.3 Electrochemical treatment

To perform the electrochemical oxidation, an Autolab Potentiostat Galvanostat PGSTAT30 was used. With this device a cyclic voltammetry program was utilised to carry out different analyses with blank and dye solutions.

Analyses were carried out in an undivided cell with volume of $0,2 \text{ dm}^3$. The cell holding dye solution can be seen in Figure 5. The electrochemical process was performed with three electrodes: a working electrode, a reference electrode and a counter electrode. The reactions take place in the working electrode. The diameter of the reaction place was 2 mm. The metal of the working electrode was from platinum. As a reference electrode, Ag/AgCl was applied. The electrolyte inside reference electrode was 3M. The role of the counter electrode was to give the electrical current and it was made out of platinum.

Nitrogen was conducted in the electrolyte solution at least for five minutes between the analyses to ensure there was no oxygen present in the solution. During the analyses nitrogen was conducted in the air above the solution surface to maintain non-oxygen conditions.

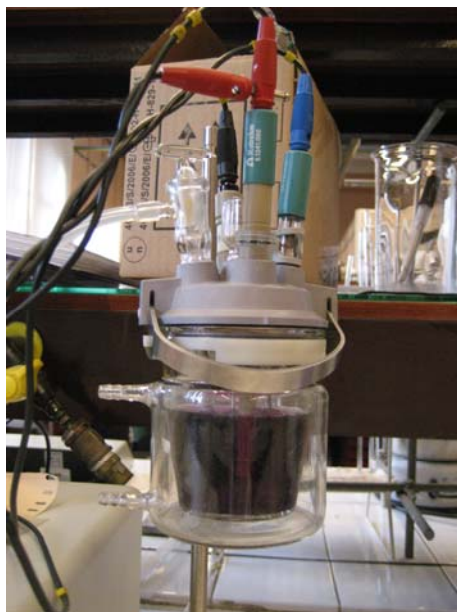


FIGURE 5. An undivided cell for electrochemical oxidation process.

4.3.1 Tests with Blank solution

The effects of different experimental parameters were tested with water diluted blank solution in order to see how these affect the results. Each parameter was tested several times to confirm that different parameters will not cause interference on the final results. There will be more discussion on the tested parameters later.

Most of the analyses were performed with two scans, step potential at 0,00244 V and scan rate at 0,05 V/s. Nitrogen input was generally five minutes between analyses. Whenever a magnetic mixer was applied the speed was set on 500 RPM.

The first cleaning technique for the working electrode included simply wiping of the electrode surface between analyses. The second cleaning technique contained three stages. First, the electrode surface was wiped with a cloth. After this, the electrode was rinsed with three different solvents: toluene, alcohol and water (in this order).

For the final infrared spectrometer analyses two different dye solutions were oxidized for 24 hours. One dye solution was water diluted and the other was dimethyleformamide diluted. Nitrogen was conducted to the air space in the cell to ensure non oxygen conditions during analyses. After 24 hours of oxidation, the solutions were evaporated to prepare the tablets for the FTIR analysis.

4.3.2 pH and conductimeter

In this study a Crison pH meter and a conductimeter were used to measure these parameters. The model of conductimeter was 522 and for pH meter it was GLP21.

When calibrating the pH meter original Crison buffer solutions were applied (pH 7.00 and 4.01). pH meter was calibrated every day before the use.

pH was measured in each pre-treatment before electrochemical oxidation as well as before and after electrochemical oxidation to see if the treatment had had some impact on this parameter. Conductivity was measured before and after oxidation to see if there had been any changes due to electrochemical oxidation.

5 RESULTS AND DISCUSSION

5.1 Concentration of the dye solution during the experiment

The maximum absorbance for Cibacron Violet appeared at the wave length 550 nm. Concentration of the water diluted dye solution was measured during the different stages of the research (Figure 4). To be able to follow the concentration changes, a calibration line was created (APPENDIX 1). With the calibration line it was possible to get the exact concentration when the absorbance of the solution was known.

The dye solution diluted slightly due to procedures in the course of the study. The concentration changes are presented in Figure 6. The stages in which the concentrations were measured, and the correspondence with different line colours can be detected from Table 1.

From the original concentration 0,1 g/l the concentration diluted into the level of 0,085 g/l . Before oxidation the concentration reached the level of 0,06 g/l. Nevertheless, the changes in the concentrations were minor and presumably did not have a major impact on the results.

TABLE 1. The correspondence with different line colours for Figure 6.

Line colour	Analysis stage
Blue	In the beginning*
Black	After pH adjustment
Brown	After hydralization
Pink	After pH and conductivity adjustment
Green	After oxidation

* before pH adjustment

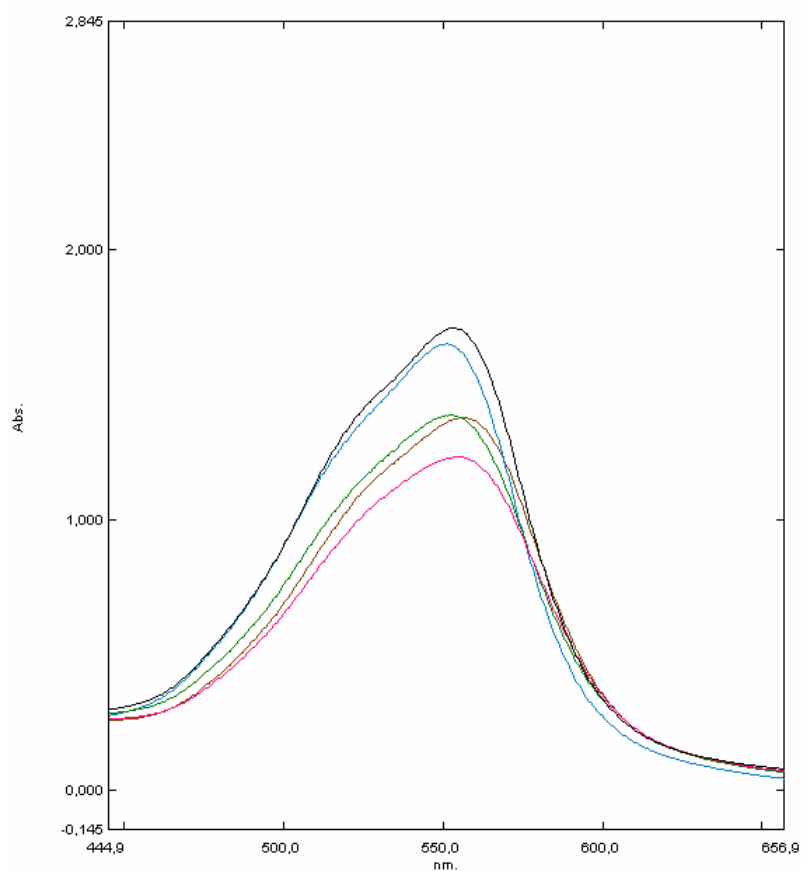


FIGURE 6. Concentrations of the water diluted dye solution during the study

The spontaneous concentration changes in oxidized dye solution were supervised for 12 days (Figure 7.). During this time the concentration went up from 0,1 g/l to the level of 0,12 g/l. These changes of concentration are probably due to the slight evaporation of the solution.

In Figure 7 the green line is a result of the analysis on day 1. The black line is measured on day 6 and the blue line is measured on day 12.

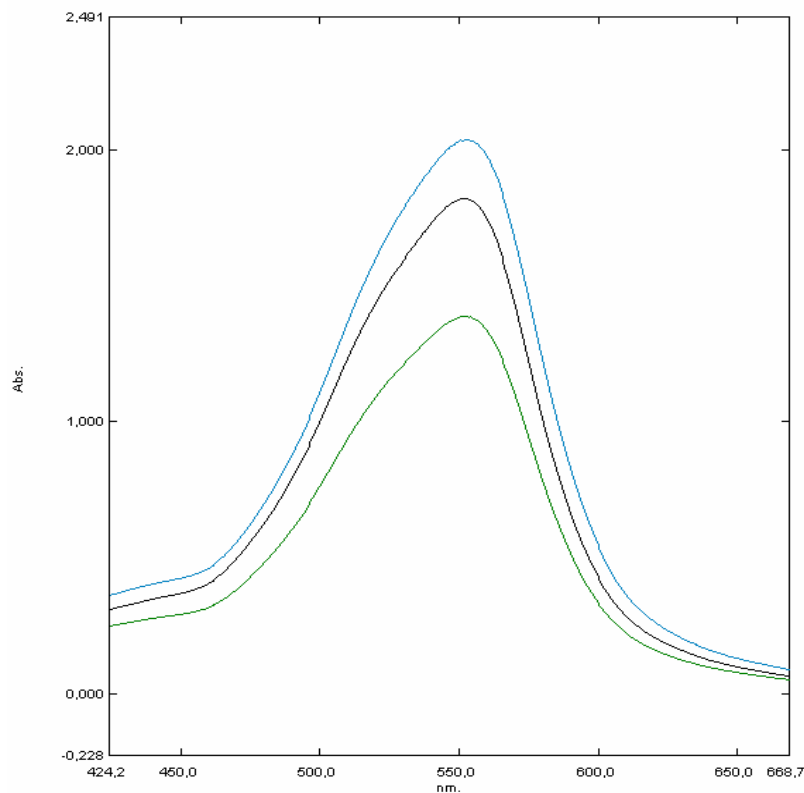


FIGURE 7. Spontaneous concentration changes on water diluted dye solution.

5.2 Changes in the chemical structure of the dye

The characterisation of the chemical structure was challenging due to the feature of the evaporated dye solution powder. When preparing the tablets for the FTIR analyses the same mass of the dye could not be used at every stage because the spectra achieved with the same mass were not always in good quality.

Figure 8 illustrates FTIR spectra for water diluted dye solutions. A red spectrum is a result from the dye solution prepared in the beginning of the process. The pH of the

solution was 12 and the concentration of the dye was 0.1 g/l. A blue spectrum is a result from the dye solution after electrochemical oxidation.

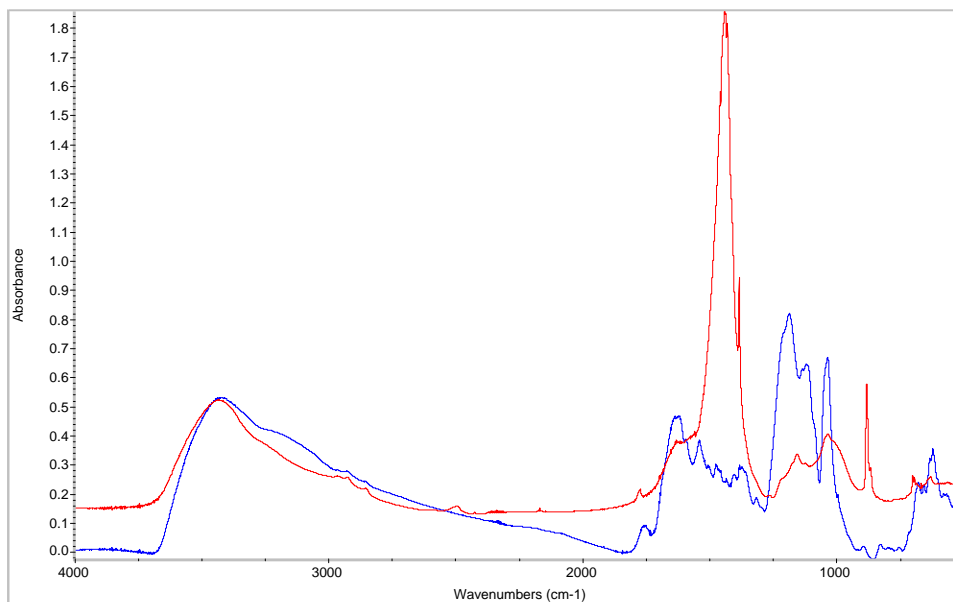


FIGURE 8. Infrared spectrometers for water diluted dye solution.

In Figure 8. it can be detected that there has been changes in the chemical structure of the dye. Many bands from the red spectrum disappeared after electrochemical oxidation and new bands naturally appeared in the blue spectrum (APPENDIX 3). It seems that either the whole complex of triazine and the chemical groups bonded with that have been detached due to electrochemical oxidation process or the reactions that took place have happened in the chemical group bonded with triazine. There is a group of OC_6H_5 and NH_2 (mixture) attached to triazine. Because new bonds between nitrogen ions have developed, it is more likely that the whole triazine complex has detached from the rest of the chemical.

The changes in the chemical structure of the dye can not be seen as clearly when DMF diluted dye solutions were analyzed with an FTIR device. Only few bands appeared in the spectrum analyzed after electrochemical oxidation (APPENDIX 4). The

spectra from DMF diluted dye solutions can be seen in Figure 9. As can be seen from Figure 9, many changes did not seem to occur after electrochemical oxidation. This could be detected more clearly when the two spectra were set on the same absorbance level. The peaks that appeared in the two spectra were exactly at the same wavenumbers, which indicates that there had not been changes in the chemical structure of the dye.

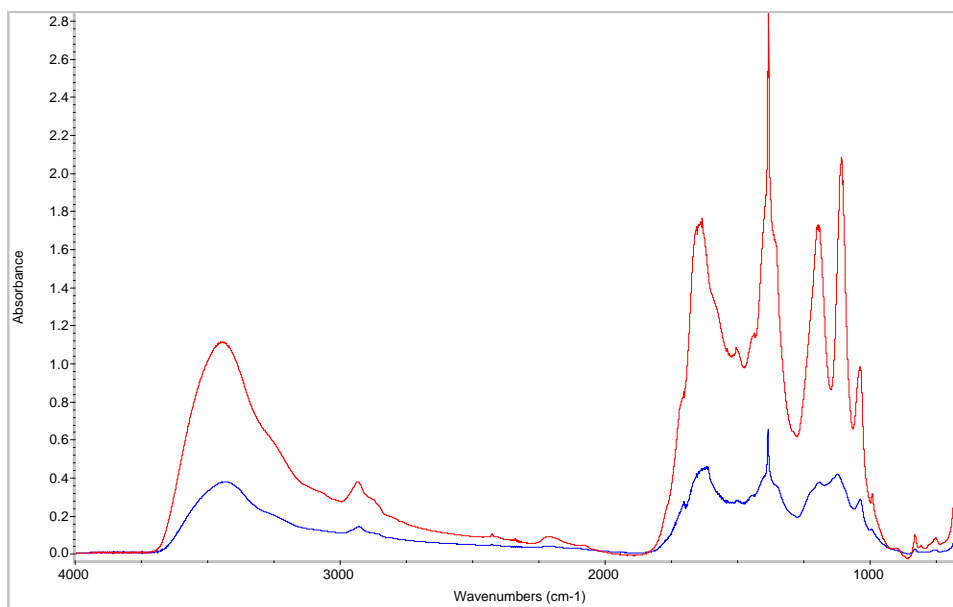


FIGURE 9. Infrared spectra for DMF diluted dye solutions.

In Figure 10 the changes in chemical structure of the dye can be seen. It can be noticed that there were changes also before the electrochemical oxidation (APPENDIX 5). It was expected that most of the changes occur after electrochemical oxidation, not before. Table 2. clarifies at which stage each of the different spectra have been analysed.

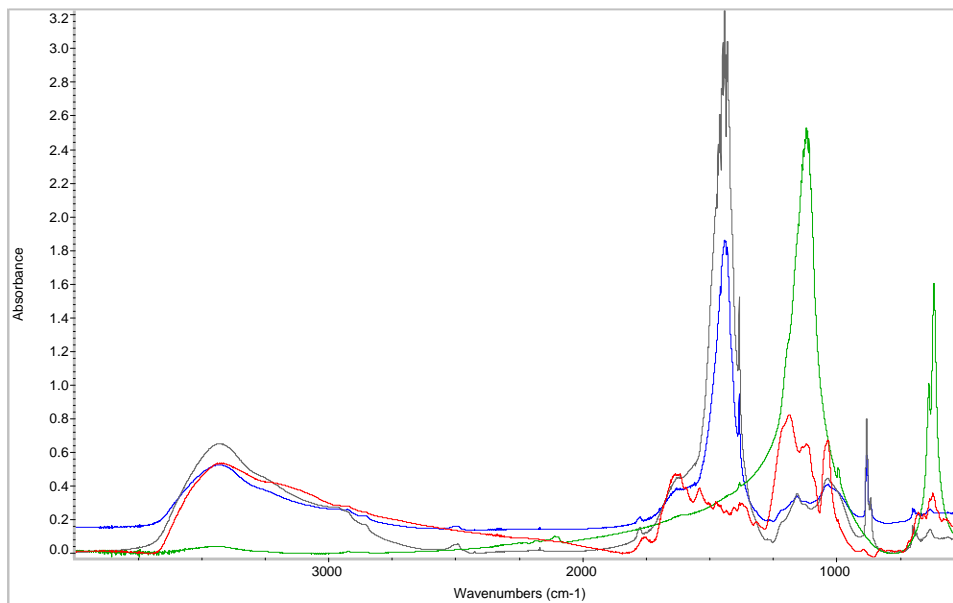


FIGURE 10. Chemical changes in water diluted dye solution

TABLE 2.

Line colour	Stage
Blue	Beginning, pH 12, concentration 0,1 g/l
Grey	After hydralization
Green	After pH and conductivity adjustment
Red	After oxidation

There were no changes in the chemical structure of the dye before or after hydration. When pH and conductivity were adjusted to the required level (considering oxidation process) there seemed to be major changes in the chemical structure. The bonds between carbon and hydrogen or between carbon and oxygen atoms seemed to break. Also, some methyl bonds were broken due to the treatment.

After electrochemical oxidation new changes took place. There were signs of ring vibration. New bonds appeared to develop between carbon and oxygen atoms and between two carbon atoms. An aliphatic carbon attached to another carbon atom with a

double bond appeared to the spectrum and this possibly means that the structure of benzene ring has broken. Sulphur dioxide could also be detected from the spectra after electrochemical oxidation.

5.3 Electrochemical oxidation results with water diluted dye solution

In this study the results achieved with cyclic voltammetry are not in standard scale. In order to convert the results in standard scale, Nernst Equation is required.

$$1) E_{\text{HNE}}(\text{AgCl}/\text{Ag}) = E^0(\text{AgCl}/\text{Ag}) + (RT/mF) * \ln [\text{Cl}^-]$$

$$E^0(\text{AgCl}/\text{Ag}) = 0,2221 \text{ V}$$

$$R = 8,314 \text{ J/Kmol}$$

$$T = 25 \text{ }^\circ\text{C} = 298,15 \text{ K}$$

$$m = 1$$

$$F = 96485,338 \text{ C/mol}$$

$$[\text{Cl}^-] = 3 \text{ M}$$

$$E_{\text{HNE}}(\text{AgCl}/\text{Ag}) = 0,2221 \text{ V} + [(8,314 \text{ J/Kmol} * 298,15 \text{ K}) / (1 * 96485,338 \text{ C/mol})] * \ln 3 \\ = 0,2503 \text{ V}$$

An example with 2V:

$$2) E_{\text{HNE}} = V + E_{\text{HNE}}(\text{AgCl}/\text{Ag}) = 2 \text{ V} + 0,2503 \text{ V} = 2,2503 \text{ V}$$

→ When having, for example, 2 V at the result scale it would equal 2,2503 V on a standard scale.

The effects of different parameters tested varied. All of them (1-7) were tested several times.

1) various times of nitrogen input into the solution (from five to fifteen minutes)

2) two different cleaning techniques for the working electrode

- 3) various speeds in scanning (from 0.05 to 1 V/s)
- 4) various analyses orders and starting points
- 5) various voltage zones and directions of the scans
- 6) using/not using magnetic mixer
- 7) various quantity of scans (between two and ten)

From the tested parameters, points 1 to 2 did not seem to have any effect on the results. Using a faster scan rate (3) the voltammograms achieved were slightly noisier but the difference was not major. Various analyses orders or starting points of the scans did not give any different results.

Various quantities of scans showed difference in results. With only two scans all the reactions could not be seen as clearly as with ten scans. Therefore the analyses measured afterwards were accomplished with ten scans.

Various voltage zones had a clear effect on the voltammograms. High voltage zones (over 4 volts) caused generation of gas which had a negative impact on the results. The gas bubbles resulted in a noisy voltammogram. In Figure 11 this effect can be noticed. In Figure 11 the cyclic voltammetry analysis was performed between zero and nine volts. On average, the analyses with lesser voltages were performed before the analyses with higher voltages. This was due to the potential appearance of reaction products or side products with higher voltages. The direction of the scan did not show any difference on the results.

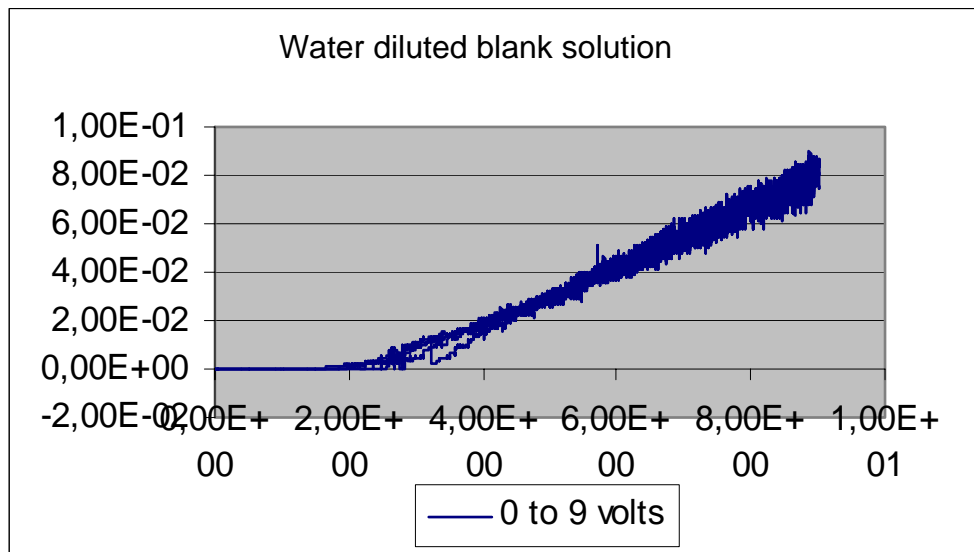


FIGURE 11. Voltammogram for water diluted blank solution with high volts

A magnetic mixer caused noise on the voltammograms as expected. This was, nevertheless, such a minor noise that in many analyses, the magnetic mixer was applied for the positive effects it had. With the magnetic mixer the generation of gas did not have such a major negative effect on the results because it moved the bubbles away from the surface of the working electrode. Figure 12 shows a voltammogram from a water diluted blank solution of which one is with a magnetic mixer (blue line) and the other without (pink line). In this analysis, ten scans were performed.

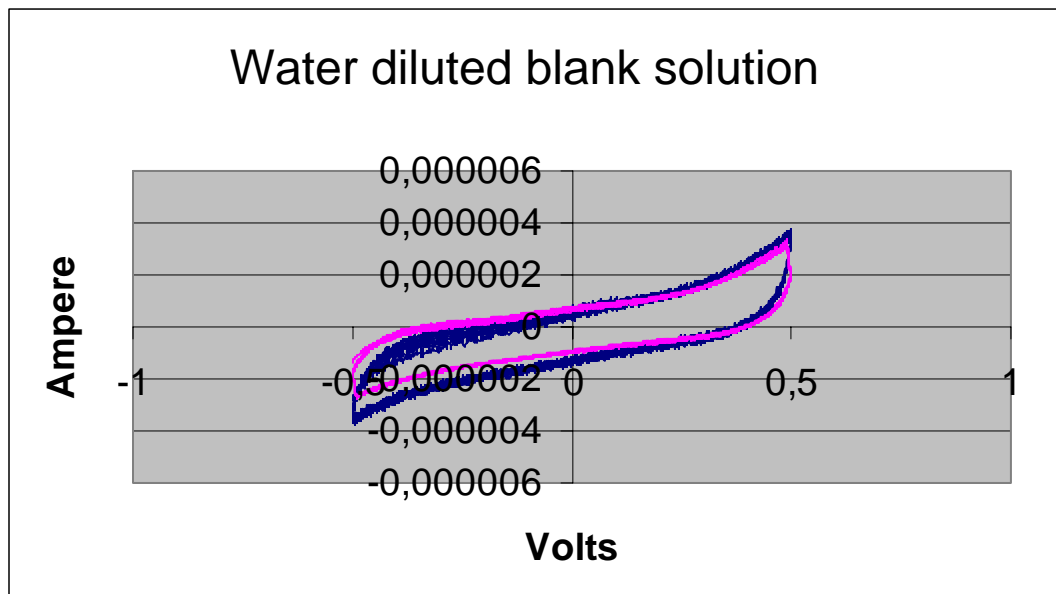


FIGURE 12. Voltammogram with and without magnetic mixer

The voltage zone in which the ten scans took place was from -0.5 to 0.5 volts. On this voltage zone, no reactions were detected.

The problem with all the analyses was that zone free from reactions could not be found with the water diluted blank solution. With the water diluted blank solution there was reaction even at the lowest voltages; this can be seen in Figure 13. This fact made it impossible to see the reactions that took place on behalf of the reactive dye.

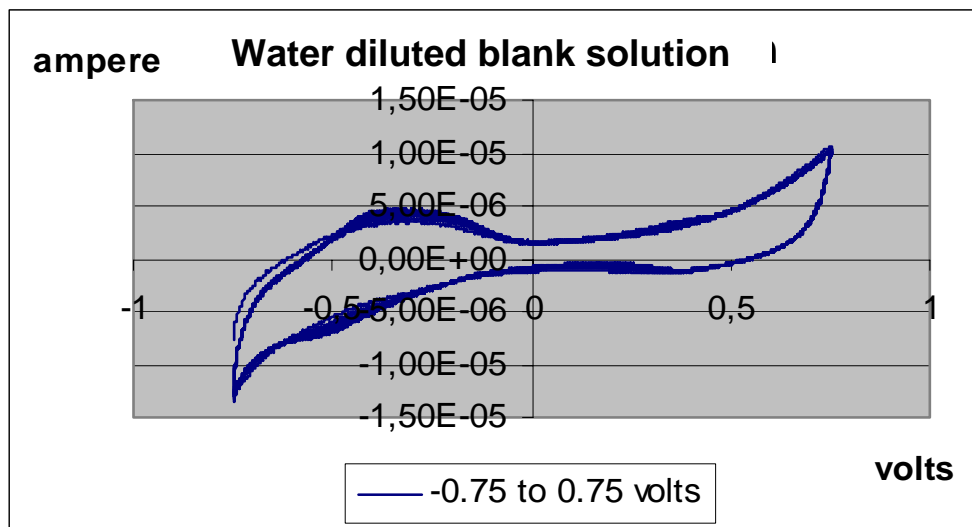


FIGURE 13. Reaction with water diluted blank solution

In Figure 13 the reactions that took place on these voltages can be seen at -0.3 volts and at -0.5 volts. With ten scans the reactions could be seen clearly. Earlier, when the same voltage zone was applied, the reactions could not be detected in the analyses.

5.4 Electrochemical oxidation results with other solvents

In order to achieve proper results from electrochemical oxidation, different solvents were tested. After solubility tests with the dye and with sodium sulphate anhydrous, it became clear that ethanol could not be used as a solvent for electrochemical oxidation. The solubility of sodium sulphate anhydrous was less than 0.01 g/l, leaving the conductivity as low as 4.08 $\mu\text{S}/\text{cm}$. The solubility of the dye was nearly zero.

With dimethylformamide the concentration of the dye reached the same level as with a water diluted dye solution (0.1g/l). The salt solubility was not as good as with water but the conductivity level of the dimethylformamide diluted dye solution used for electrochemical oxidation was 16.81 $\mu\text{S}/\text{cm}$. The conductivity of the dimethylforma-

midly diluted blank solution was $2.07 \mu\text{S}/\text{cm}$. Due to these solubility test results, only dimethylformamide diluted solutions were oxidised electrochemically.

With dimethylformamide the reactions of the reactive dye, Cibacron Violet, could be clearly detected in all voltage zones. In Figure 14 the reaction that the dye has caused can be seen. These analyses were measured with voltage zone from 0 to 1 volts and with the scan rate $0.05\text{V}/\text{s}$. A magnetic mixer was not used. Ten scans were measured both with a blank and with a dye solution.

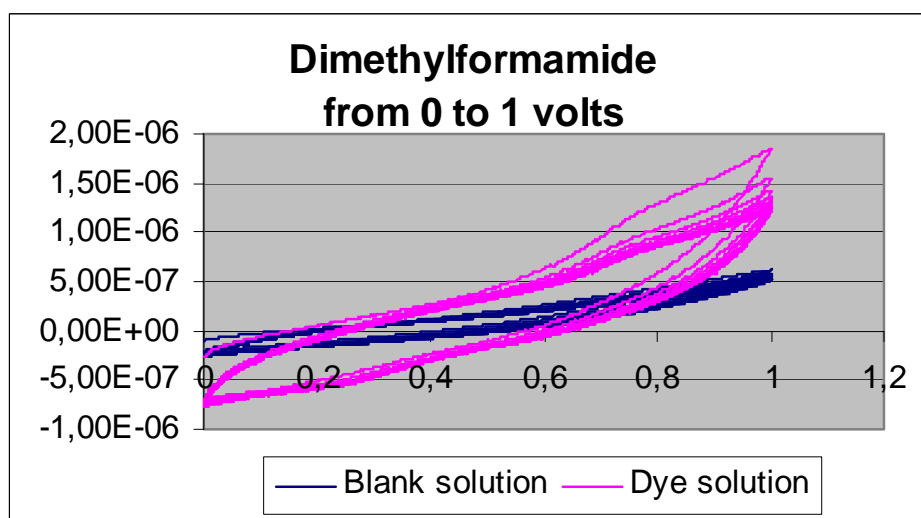


FIGURE 14. Voltammograms from dimethylformamide solutions

As the voltage zone got wider it also became easier to see the reactions that took place. With dimethylformamide the generation of gas was not an issue. With high voltages (seven volts), when the voltammograms from the water diluted solutions were noisy, using dimethylformamide instead no gas generation could not be detected, neither in the voltammogram nor in the solution itself.

5.5 Conductivity and pH results

The electrochemical oxidation distinctly appeared to have an impact on the conductivity of the electrolyte solution. Electrochemical oxidation raised the conductivity. This could be detected with short analyses series and, above all, after the 24 hour electrochemical oxidation. After 24 hours of electrochemical oxidation the conductivity of the solution had doubled.

On pH the electrochemical oxidation did not seem to have as clear an effect as in conductivity. On a few occasions the pH raised a little but the same effect could not be detected with all the analyses. On many occasions, the pH did not convert at all. After 24 hours of electrochemical oxidation the pH had raised only 0.2 units.

5.6 Improvements in the conditions of the electrochemical bulk oxidation

In electrochemical oxidation, it is extremely essential to avoid contamination. Electrochemical oxidation device is sensitive and reacts easily if there are organic compounds (contaminants) in the cell. Chlorine is also a substance that can cause interference on the results. Therefore, all the instruments used for electrochemical oxidation must be handled with a chemical that eliminates the unwanted organic compounds.

The instruments used in this study had been handled with a chemical that eliminates organic compounds. In spite of that, there were contaminants in the water diluted solutions. In this study, the origin of the contaminants is not entirely certain.

It is essential to clean the electrodes between the analyses. Otherwise there can be reaction products from the previous analyses on the surface of the working electrode. To avoid contamination, the electrodes should be cleaned with a cloth that does not

leave any residuals. Rinsing the electrodes with some solvents can also be functional.

6 CONCLUSIONS

Textile industrial wastewaters acquire efficient water purification. In the future, many different techniques to purify the wastewaters are probably introduced because the reuse of water is becoming more and more important. One way to try to reach the highest reuse in wastewaters is to use electrochemical techniques. These techniques are not well known, at least yet. One of the biggest issues when using electrochemical techniques is electricity. To purify wastewaters on large scale the amount of electricity needed is quite big. This is one of the reasons why electrochemical techniques have not become very popular. However, the results of this study seem to indicate that electrochemical oxidation is a good way to purify textile industrial wastewaters.

The identification of the changes in the chemical structure of the dye turned out to be a challenging task. To achieve good infrared spectra, different amounts of dye powder had to be tested. Nevertheless, good spectra were not achieved in every case and this made the identification of the chemical structure difficult. More time would have been required to achieve more reliable results.

When using another solvent, DMF, on electrochemical oxidation, the reactions that took place on behalf of the reactive dye could be detected. When working with dimethylformamide diluted solutions, the generation of gas and the bubbling followed by the gas generation was not an issue. This was presumably due to lower conductivity. The dimethylformamide diluted solution had only one thousandth of the conductivity in water diluted solutions. In spite of the reactions detected in voltammograms there were no clear changes in the chemical structure of the dye in FTIR results. DMF is not an easily evaporative liquid and the quality of the dye powder achieved through

evaporation was slightly questionable.

The contaminations that appeared in the water diluted solutions were most likely from the water itself and from the chemicals that were used in the pre-treatments before the electrochemical oxidation. Both sodium sulphate anhydrous and sodium hydroxide contained some chlorine and phosphate compounds. The problems with these took a lot of time and yet it did not lead to good results.

Textile industrial wastewaters treated with electrochemical oxidation are effectively cleaned. To define more accurately what occurs in the chemical structure of the dye during this electrochemical oxidation process, further research is required.

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APPENDICES

Calibration line used to determine concentrations during this study (APPENDIX 1)

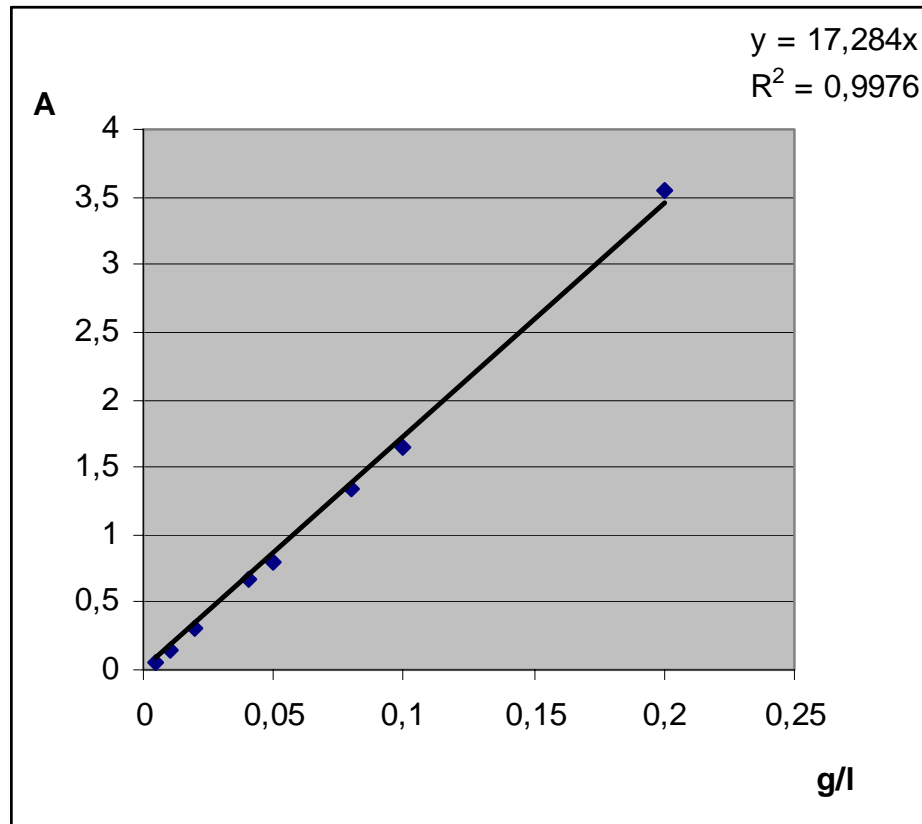
UV-V spectra of different concentrations for calibration line (APPENDIX 2)

Specific band regions changed in water diluted dye solutions (APPENDIX 3)

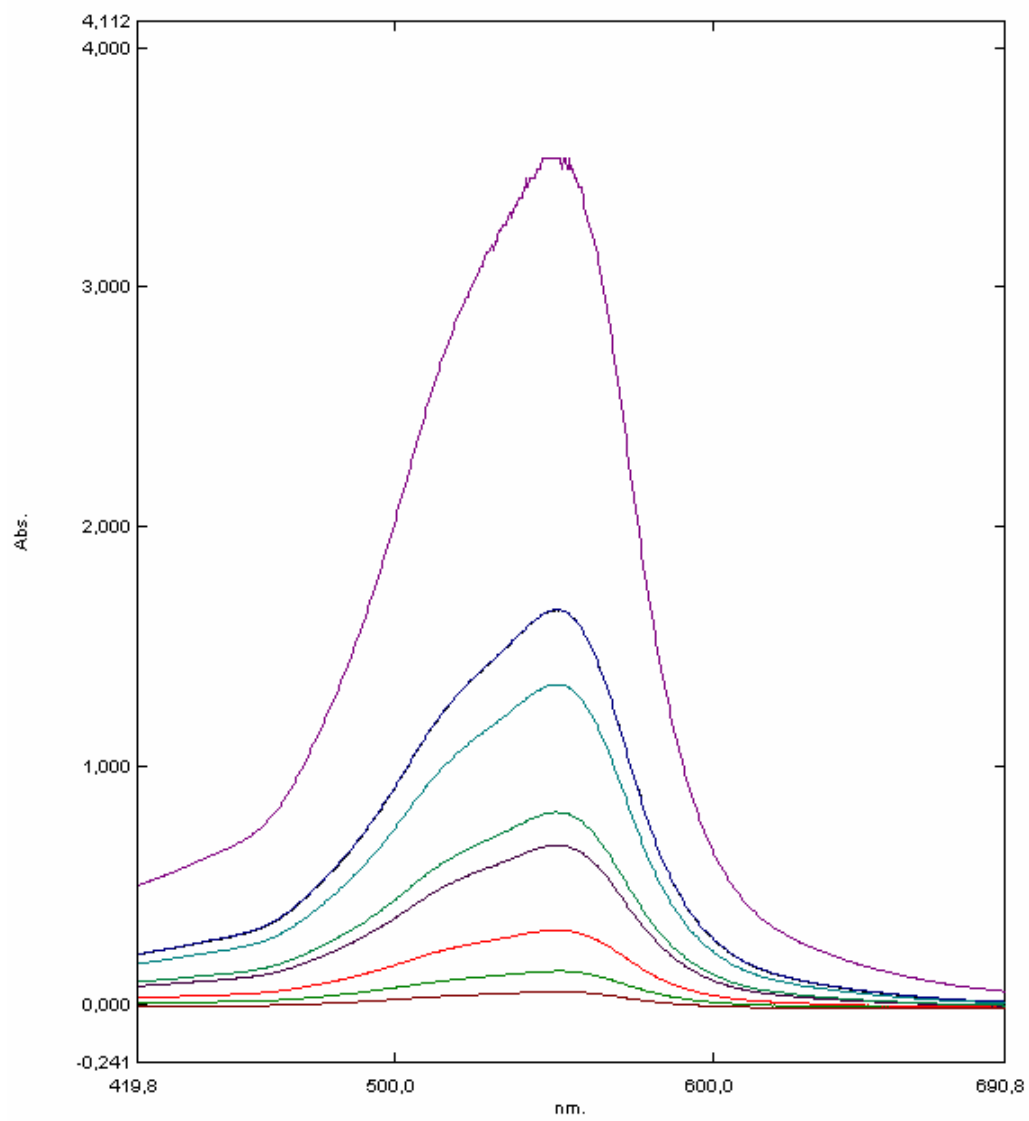
Specific band regions changed in DMF diluted solutions (APPENDIX 4)

The band regions that changed in different stages of electrochemical oxidation process (APPENDIX 5)

APPENDIX 1



APPENDIX 2



APPENDIX 3

FIGURE 8	Wavenumber (cm ⁻¹)	Type of compound
Bands disappeared	1440-1435	C-CH ₃
	1385	
	1180-1160	N,N-Disubstituted sulphonamide
	1120	-C-N- stretch, RCH ₂ NH ₂
	885-869	C-H bend, 1,2,4-Trisub. benzene
	870	C-H bend, pentasubstituted benzene deriv.
New bands appeared	1645-1610	ortho OH (or NH ₂) aryl
	1570-1520	-N-NO ₂ , asym. Stretch, Alkyl nitramine
	1200-1100	-C-N stretch, R

APPENDIX 4

FIGURE 9	Wavenumber (cm ⁻¹)	Type of compound
New bands appeared	1520-1490	-NH ₃ ⁺ sym.bend, Amino acid hydrochloride and zwitterion
	810-800	C-H bend, 1,2,3,4-Tetrasubstituted benzene deriv.

APPENDIX 5

FIGURE 10	Wavenumber (cm^{-1})	Type of compound
Changes after pH and conductivity adjustment		
Bands di- sappeared	1500-1390	-CH ₃ , asym.bend, Alkyl benzene deriv.
	1390-1380	-CH ₃ , sym.bend, gem-Dimethyl group
	1070-950	-C-O-C- sym.stretch, C=C-O-C in vinyl and aryl ethers, etc.
	890-870	-
	870-855	C-H bend, 1,2,4,5-Tetrasubstituted benzene deriv.
	701-694	C-H bend, Monosubstituted benzene deriv.
	695-690	-
	690-680	-O-N=O bend, RCH ₂ -O-N=O (cis)
New bands appeared	1145-1100	-C-O-C asym.stretch, Aliphatic ether
	1000-990	-C-D bend, methane-d ₄
	650-630	-C-S- stretch, RCH ₂ -S-
	630-605	-C-S- stretch, R ₁ R ₂ HC-S-
Changes after electrochemical oxidation		
New bands appeared	1660-1600	-C=C- stretch
	1600-1590	Ring vibration, Aromatic hydrocarbon
	1510-1560	-N-H bend(?), N-monosubstituted amide (dioxane soln)
	1485-1470	-
	1420-1400	-C=C-H in-plane, C-H bend, R ₁ HC=CHR ₂ (cis)
	1380-1365	-CH ₃ sym.bend, Methylbenzene deriv.
	1200-1150	SO ₂ stretch, Sulphonate and sulphate
	1065-1000	-C-O-C- sym.stretch, C=C-O-C in vinyl and aryl ethers, etc.