

Chemical Engineering Journal 119 (2006) 127–133

Chemical Engineering Journal

www.elsevier.com/locate/cej

# A comparative study of platinised titanium and niobe/synthetic diamond as anodes in the electrochemical treatment of textile wastewater

Anastasios Sakalis<sup>a</sup>, Konstantinos Fytianos b,\*, Ulrich Nickel<sup>c</sup>, Anastasios Voulgaropoulos<sup>a</sup>

<sup>a</sup> *Laboratory of Analytical Chemistry, Chemistry Department, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece*

<sup>b</sup> *Laboratory of Environmental Pollution Control, Chemistry Department, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece*

<sup>c</sup> *Institute of Physical Chemistry, University of Erlangen-Nuremberg, Egerlandstrasse 3, D-91058 Erlangen, Germany*

Received 17 October 2005; received in revised form 20 February 2006; accepted 24 February 2006

## **Abstract**

An electrochemical method for wastewater treatment in the textile industry based on an electrolysis process is discussed in this paper. In a laboratory scale electrochemical cell made of Plexiglas, carbon fleece is used as a cathode while two materials such as niobe/synthetic diamond (Nb/D) and platinised titanium (Pt/Ti) are tested as anodes. Synthetic samples, containing specific amounts of four reactive azodyes and electrolytes diluted in tap water, are treated using Pt/Ti. Parameters affecting the procedure such as the nature and the quantity of the electrolyte, the pH and the applied potential are researched and discussed. Temperature, current and pH are measured on line. Samples are taken at appropriate intervals during the process and UV–vis spectra are received. Real wastewater samples are treated with no further addition of electrolytes. Biochemical oxygen demand (BOD5), chemical oxygen demand (COD), total organic carbon (TOC), energy consumption and efficiency of the anodes, as well as the chloride (Cl−) and hypochlorite (ClO−) concentrations, are measured using both Pt/Ti and Nb/D as anodes, comparing their efficiencies. Color removal up to 90% is achieved resulting in practically colorless final wastewater, while BOD<sub>5</sub>, COD and TOC are decreased up to 49.6%, 93.3% and 52.4%, respectively, using Nb/D.

© 2006 Elsevier B.V. All rights reserved.

*Keywords:* Azodyes; Electrochemical treatment; Textile wastewater; Degradation; Electrolysis; Decoloration

## **1. Introduction**

There is a great amount of wastewater in the textile industries as a result of the dyeing and finishing processes and this water is very difficult to treat. It is strongly colored and has high values of pH, temperature and COD, while it shows low biodegradability [\[1,2\]. M](#page-6-0)oreover, it is claimed that textile dyestuffs not only act as allergens, but also exhibit toxic, even mutagenic or carcinogenic properties [\[3–6\].](#page-6-0) The removal of dyes is therefore a challenge to the textile industry and of great importance for the protection of the environment.

Textile industry wastewater is usually treated by conventional methods such as adsorption in polyelectrolytes [\[7\],](#page-6-0) chemical oxidation or reduction [\[8\]](#page-6-0) and biological degradation [\[9–13\].](#page-6-0) Adsorption does not solve the pollution problem, but shifts it into solid waste disposal, while chemical treatment produces final wastewater contaminated with significant quantities of chemical reagents. Biological treatment, which is the main procedure used, causes sludge formation and additionally it is not able to degrade the pollutants completely, since it is known that huge organic molecules with many phenyl rings are hard to biodegrade, mainly due to stereo chemical interferences. Recently, novel methods of textile wastewater treatment have been developed [\[14\].](#page-6-0) Ozonation is quite effective in decolorizing textile wastewater, but the cost of the procedure is high and additional problems arise such as increased pollution of wastewater caused by ozone and high final pH values [\[15–17\].](#page-6-0) Combined processes such as photochemical treatment [\[19\]](#page-6-0) and ozone/chemical treatment, resulted in better efficiency and quicker decoloration, however, the cost of such approaches is still high and is not equally effective to all of the azodyes [\[18,20\].](#page-6-0) Furthermore, the addition of chemical reagents and the production of several radicals cause insignificant reduction of TOC and COD values producing colorless though slightly degraded final wastewater [\[1,18,19\].](#page-6-0)

*Abbreviations:* BOD5, biologically oxygen demand (measured after 5 days); COD, chemically oxygen demand; TOC, total organic carbon; Pt/Ti, platinated titanium; Nb/D, niobe/diamond

<sup>∗</sup> Corresponding author. Tel.: +30 2310997873; fax: +30 2310997873. *E-mail address:* [fyti@chem.auth.gr](mailto:fyti@chem.auth.gr) (K. Fytianos).

<sup>1385-8947/\$ –</sup> see front matter © 2006 Elsevier B.V. All rights reserved. doi[:10.1016/j.cej.2006.02.009](dx.doi.org/10.1016/j.cej.2006.02.009)



Very promising are the electrochemical processes for the treatment of textile wastewater. The dyes are destroyed by direct anodic and cathodic processes on the electrode surfaces together with indirect anodic oxidation and cathodic reduction. These processes are realized by oxidants such as hydroxyl radicals, ozone and hypochlorite anions on the onehand as by several reductants like thiosulfate anions  $(S_2O_3^{2-})$  in cases where H2SO4 is used as electrolyte on the other hand. Electrochemical methods have been successfully applied in the treatment of industrial wastewater, however, large quantities of electrolytes are added in order to obtain satisfactory results[\[21–27\]. I](#page-6-0)n previous research undertaken by our group, preliminary experiments showed that azodye wastewater could successfully be treated with no further addition of electrolytes, even in a pilot plant scale electrolytic cell [\[33\].](#page-6-0) Furthermore, the use of separation techniques such as liquid chromatography (LC) coupled with mass spectrometric detector (MS), gave some initial evidence concerning the intermediate and final degradation products[\[32\].](#page-6-0)

In the present paper, more extensive experiments are performed in order to evaluate the influence of significant parameters such as electrolyte, pH and applied potential using carbon fleece as cathode and platinised titanium (Pt/Ti) as anode. Synthetic samples of four multi-soulfonated reactive azodyes, used in the textile industry, are treated [C.I. names: Reactive Orange 91 (*M*<sup>r</sup> = 747), Reactive Red 184 (*M*<sup>r</sup> = 855.5), Reactive Blue 182  $(M_r = 863.5)$  and Reactive Black 5  $(M_r = 947)$ ]. At a further stage, under optimal conditions a novel material well known for its high stability and significant conductivity such as niobe/diamond (Nb/D) [\[31\]](#page-6-0) is compared to Pt/Ti in real wastewater and the most significant environmental parameters are evaluated and discussed.

## **2. Materials and methods**

#### *2.1. Materials and reagents*

Carbon fleece is a Sigatherm PR201-16 model, obtained from SGL Carbon Group (Germany). The anodes made of platinated titanium and niobe covered with boron doped diamond surface, are obtained from Metakem GmbH (Germany). The laboratory scale electrolytic cell was made from Plexiglas, obtained from the Institute of Physical Chemistry, University of Erlangen (Germany).

All multi-sulfonated azodyes used are of commercial purity grade. Reactive Orange 91, Reactive Red 184 and Reactive Blue 182 are obtained from Ciba Co. (Switzerland). Reactive Black 5 is obtained from DyStar Textilfarben GmbH & Co. (Germany KG). All salts used as electrolytes, as well as reagents used for measurements according to Standard Methods are of analytical purity grade obtained from Merck (Darmstadt, Germany). Tap water is used for all synthetic solutions in electrochemical treatment, for better simulation with real wastewater. Doubly distilled water is used for all measurements according to Standard Methods [\[36\].](#page-6-0)

#### *2.2. Instrumentation*

A laboratory scale electrolytic cell made of Plexiglas with a capacity of  $500 \text{ cm}^3$  is used. The procedure is based on batch operation and the aeration of the solution is achieved from the bottom of the electrolytic cell, resulting in better and quicker approach of the dye molecules onto the electrode surface. Furthermore, aeration provides adequate quantities of  $O_2$ , which could be oxidized and produce sufficient quantities of  $O_3$  on the anode surface. The aeration is provided either by central airflow or by compact air pumps. The arrangement of the electrodes consists of three cathodes and two anodes accommodated in alternate order with a distance of 2 cm between them ([Fig. 1\).](#page-2-0)

The carbon fleece plate is a specially treated and modified carbon with dimensions  $12.0 \text{ cm} \times 7.0 \text{ cm} \times 0.3 \text{ cm}$  with large porosity and active surface area, and low density and weight, because of its loosely woven structure of low density. This type of electrode shows a great stability, acid, base and redox resistance, is not easily deactivated and is easily cleaned and stored.

Two materials are tested as anodes, platinated titanium with  $50 g Pt/m<sup>2</sup>$  and modified niobe substrate coated with a thin film of diamond doped with boron atoms.

Platinum is a material with rather good characteristics, but it is very expensive to use as anode. Instead, the much cheaper Pt/Ti can be used, presenting similar effectiveness, stability, easy cleaning and storage. The anode is constructed by using three parallel solid cylindrical wires settled on a plastic frame, which establish a high current density and good mixing of the solution in the electrochemical cell. The diameter and length of wires are 0.12 and 11.5 cm, respectively.

The Nb/D electrode is the most expensive, but nevertheless the most promising electrode. Its body is made of niobe covered by a thin layer of synthetic diamond, doped with boron atoms. It is a very electroactive and stable material in all redox, acid and alkaline media. The shape of the electrode is a solid net with dimensions of  $14.9 \text{ cm} \times 6.9 \text{ cm} \times 1.0 \text{ cm}$ . The required applied potential is provided by a homemade power supply, in the range 0–30 V, which is connected with an amperometer (0–20 A), indicating the current simultaneously [\(Fig. 1\).](#page-2-0)

Throughout the experimental work, parameters such as pH, temperature and current are measured on line. pH is measured

<span id="page-2-0"></span>

Fig. 1. The electrolytic cell.

using Hanna Instruments pHmeter, while the current value is measured by the amperometer accompanying the power supply. A Jasco V-530 spectrophotometer using cells with 1 cm path length is used for UV–vis spectra measurements. COD, BOD<sub>5</sub>, chlorides and hypochlorites are measured according to Standard Methods [\[36\]. F](#page-6-0)inally TOC is measured using a Shimanzu TOC-V CSH, Total Organic Carbon Analyzer.

#### *2.3. Experimental procedure*

Synthetic samples containing a certain concentration of a specific azodye as well as a suitable concentration of electrolyte are used for the evaluation of the experimental parameters. All samples are diluted in tap water (Table 1) for better simulation of the real wastewater. Experiments are performed in acidic (pH 2), neutral (pH 7) and basic (pH 10) media. Nitric acid ( $HNO<sub>3</sub>$ ) and ammonium hydroxide ( $NH<sub>4</sub>OH$ ) were used for the pH adjustment. Different potential values are applied ranging from 12 to 18 V, depending on the concentration and the nature of the electrolyte presented in the wastewater. The applied potential value should combine the quickest possible rate of decoloration together with the lowest energy consumption and temperature increase. Furthermore, certain quantities

Table 1

Chemical composition and physicochemical parameters of tap water used for synthetic azodye samples (Urban area of Thessaloniki, Greece)

Chemical composition (mg/L)	
$Ca^{2+}$	98.6
$Mg^{2+}$	14.4
$Na+$	27.6
$K^+$	2.1
$NH_4$ <sup>+</sup>	$\Omega$
HCO <sub>3</sub>	342
$SO_4{}^{2-}$	16.3
$Cl^{-}$	40.0
NO <sub>3</sub>	7.2
Physicochemical parameters	
pH	7.50
Conductivity $(\mu S/cm)$	750
Total soluble solids (mg/L)	390

of several electrolytes are used, such as sodium fluoride (NaF), sodium sulfate  $(Na_2SO_4)$ , sodium chloride (NaCl), sodium carbonate ( $Na<sub>2</sub>CO<sub>3</sub>$ ), sodium acetate (CH<sub>3</sub>COONa) and phosphate buffer (Na<sub>2</sub>HPO<sub>4</sub>/KH<sub>2</sub>PO<sub>4</sub>) using platinised titanium (Pt/Ti) as anode.

Sampling is performed at specific intervals, depending on the progress of the experimental process that is indicated by the online measured values of pH, temperature and current, as well as by the decoloration rate.

Environmental parameters such as UV–vis spectra, COD, BOD5, TOC, chlorides and hypochlorites concentration are measured every 10 min. Finally, the anode efficiency and the energy consumption is estimated for both anodes during the treatment. After every treatment, both anodes and cathode are washed with tap water. Anodes are stored in a clear, dry place, while cathode is stored in HNO<sub>3</sub> aqueous solution.

#### **3. Results and discussion**

## *3.1. Type and quantity of electrolyte*

In electrochemical processes, the type and the concentration of the electrolyte are of crucial importance. Typical textile wastewater contains significant quantities of NaCl for the improvement of the dye efficiency, together with lower quantities of  $\text{Na}_2\text{CO}_3$  and phosphate buffers for pH adjustment and small quantities of  $Na<sub>2</sub>SO<sub>4</sub>$  presented mainly in tap water. The effect of these electrolytes on the electrochemical decoloration process is presented in [Fig. 2.](#page-3-0) Furthermore, the decoloration efficiency of non-electroactive electrolytes such as NaF and CH3COONa diluted in distilled water is tested, in order to clarify the extent of the direct electrochemical reactions on the electrodes surface in comparison with the indirect reactions, due to the electrogenerated products from the electrolyte present in the wastewater.

It is clear that practically no decoloration takes place when NaF or CH<sub>3</sub>COONa are used as electrolytes in distilled water. This means that direct electrochemical processes on the electrode surface in such potential value (12 V) are absent due to stereo-chemical interferences that prevent the huge dye

<span id="page-3-0"></span>

Fig. 2. % dye removal for Reactive Red 184 synthetic samples using equimolar quantities (10<sup>-2</sup> mol/L) of several electrolytes. D.w: distilled water; T.w: tap water; time of treatment: 50 min; anode: Pt/Ti; applied potential: 12 V;  $\lambda_{\text{max}}$ : 550 nm.

molecules from reaching the electrodes surface. On the other hand, treatment using only tap water results in dye removal up to 69%. This means that even low concentration of chlorides, sulfates and other anions existing in tap water result in the indirect decomposition of the dyes giving remarkable final decoloration in a relatively short period of treatment. Further addition of chlorides and sulfates leads to improved decoloration. This enhancement is mainly caused by the formation of oxidants such as chlorine, hypo-chlorites and hyper-sulfates by the oxidation of chloride and sulfate anions on the anode and, secondly of reductants such as  $S_2O_3^{2-}$ , by the reduction of sulfates on the cathode in acid-moderate alkaline pH range [\[27–30,34,35\].](#page-6-0) These primary agents can produce secondary oxidants and reductants, which continue the redox activity on organic compounds [\[27\].](#page-6-0) The addition of  $\text{Na}_2\text{CO}_3$  (pH 11) or phosphate buffer (pH 8) leads to lowering and equaling degree of decoloration respectively, because both of the above electrolytes do not produce strong oxidants or reductants, which could enhance the indirect decoloration. Furthermore, strong alkaline pH values ( $\text{Na}_2\text{CO}_3$ ) restrain the formation of oxidants (ClO<sup>-</sup>, S<sub>2</sub>O<sub>8</sub><sup>2-</sup>) and reductants (S<sub>2</sub>O<sub>3</sub><sup>2-</sup>) from chloride and sulfate anions existing in tap water, thus the decoloration efficiency is decreased [\[28\].](#page-6-0) Finally, the equimolar addition of the electrolytes results in ionic strength, ohmic drop, conductivity and current density changes, which also affect the formation of the above-mentioned electrogenerated oxidants/reductants. As a result, the indirect decoloration is restrained using  $Na<sub>2</sub>CO<sub>3</sub>$ because of high pH value, while phosphates affect the indirect decoloration to a lesser extent because of more neutral pH value (pH 8).

In Fig. 3 it is clearly shown that increased concentration of a suitable electrolyte such as NaCl, increases both the final amount and the rate of decoloration. However, high concentration of electrolyte rapidly increases the current and consequently the wastewater temperature, causing damage on the surface of the electrodes, while in the meantime high quantities of environmentally harmful hypochlorites are produced. Therefore, the lowest possible quantity of electrolyte should be used for achieving a satisfactory decoloration process together with minimum



Fig. 3. % dye removal for Reactive Red 184 synthetic samples according to the concentration of the electrolyte. Electrolyte: NaCl; time of treatment: 50 min; applied potential: 12 V;  $\lambda_{\text{max}}$ : 550 nm.

production of environmentally unfriendly chemical compounds. Concentration of NaCl at the level of 0.1 mol/L achieves a higher decoloration rate than lower concentrations as a result of the higher rate of hypochlorites production, though the final percentage of dye removal reaches about the same level for both 0.1 and 0.01 mol/L NaCl. According to [Figs. 1 and 2,](#page-2-0) the decoloration of a real wastewater depends on the concentration of chloride and sulfate anions. Since these anions exist in significant quantities in textile industry wastewater, adequate decoloration could easily be achieved with no further additions.

#### *3.2. The effect of applied potential*

The amount and the type of the electrolyte is strictly coupled with the applied voltage. High concentration of electrolyte needs low voltage, while low concentration requires higher voltage for the same result. In any case, the lowest possible potential value able to achieve satisfactory level of decoloration within a relatively short period of treatment should be applied. Higher values of voltage lead to energy loss, high temperatures and electrode damage. Concerning the real wastewater treatment, the applied potential should complete the whole process satisfactorily, without any further addition of electrolyte.

# *3.3. The effect of pH*

The pH directly affects the degradation process. Experiments in pH 2, 7 and 10 using NaCl as electrolyte, are performed for the four azodyes as seen in [Fig. 4. I](#page-4-0)t is clearly shown for all dyes that in acid-moderate alkaline pH, the degradation process is significantly faster achieving a higher degree of decoloration than in high pH values. It must be noted that  $HNO<sub>3</sub>$  in the small quantities needed for the pH adjustment cannot significantly affect the electrochemical results. It is estimated that  $HNO<sub>3</sub>$  concentration is around  $10^{-2}$  mol/L (pH  $\sim$ 2) while NaCl concentration is 0.2 mol/L, which means around 20 times less concentration. As already noted, moderate acidic-neutral pH is the optimal range for the production of some very important oxidants and reductants such as  $ClO^-$ ,  $S_2O_8^{2-}$  and  $S_2O_3^{2-}$ , which enhance the decoloration process, while in alkaline media ( $pH > 10$ ), the formation of the above-mentioned important agents is restrained

<span id="page-4-0"></span>

Fig. 4. % dye removal during the treatment of the four azodyes. Dye concentration:  $5 \times 10^{-4}$  mol/L. Electrolytes: NaCl (0.2 mol/L); applied potential: 5 V; time of treatment: 20 min; measured wavelengths:  $\lambda_{black} = 580$  nm,  $\lambda_{\text{orange}} = 453 \text{ nm}, \lambda_{\text{blue}} = 607 \text{ nm}, \lambda_{\text{red}} = 550 \text{ nm}.$ 

[\[27–30\].](#page-6-0) Thus, the enhancement of the decoloration process by chemical redox activity is optimal in the pH range between 2 and 9. This wide optimal pH range, renders the method rather versatile, in contrast to biological, chemical and ozonation methods, which need a narrow pH range for optimal efficiency [\[8–13,15–17\].](#page-6-0)

In Fig. 5, the pH process during the electrochemical treatment of Reactive Orange 91 in different initial pH values is presented. It can be seen that no matter what the initial pH of the wastewater is, the process moves slowly to a final pH value around 8 [\[27\]. T](#page-6-0)his is very important because the treated wastewater is almost neutral causing no problems to the environment. In such case no further adjustment of the final pH is required (Table 2).

The transition of the final pH to a value around 8 can be attributed to the formation of carbonate buffer via  $CO<sub>2</sub>$ . This means that mineralization takes place to some extent, which is much higher in acid pH values, since pH adjustment to pH 8 proceeds much more quickly than in alkaline initial pH as seen in Fig. 5.



Fig. 5. The pH process, during the electrochemical treatment of synthetic sample of Reactive Orange 91. Anode: Pt/Ti; applied potential: 5 V; electrolyte: 0.2 mol/L NaCl; time of treatment: 35 min; measured wavelength:  $\lambda_{\text{max}} = 453$  nm.

Initial and final values of the most important environmental parameters of electrochemically treated wastewater under optimal conditions



Time of treatment: 30 min.

#### *3.4. Electrochemical treatment of industrial wastewater*

The comparison of Pt/Ti and Nb/D, using real wastewater, without any further addition of electrolytes is presented in Fig. 6. Taking into account that the concentration of chlorides in the wastewater is only  $6.3 \times 10^{-3}$  mol/L (224 mg/L), as seen in [Table 1, h](#page-2-0)igher applied potential (18 V) is required in order to achieve a higher rate of electrogenerated oxidative and reductive products.

In a 30 min treatment period, the rate of decoloration for the two anodes is similar (Fig. 6). However, the Nb/D achieves a higher degree of decoloration (85–90%), resulting in practically colorless final wastewater. It seems that the outer film of the anode, made of boron doped synthetic diamond, provides better electrochemical properties.

The temperature and the current profiles are presented in [Fig. 7.](#page-5-0) Both temperature and current values are higher in the case of Nb/D. Higher current means that electrochemical kinetics is probably faster in the case of Nb/D electrode, while higher temperature can be attributed to the Joule effect.

Concerning the anode efficiency and the energy consumption, Nb/D demonstrates better behavior, requiring lower energy



Fig. 6. Decoloration efficiency of Nb/D and Pt/Ti, treating real wastewater. Applied potential: 18 V; time of treatment: 30 min.

<span id="page-5-0"></span>

Fig. 7. Current and temperature profiles during the treatment of real wastewater, using Nb/D and Pt/Ti as anodes. Applied potential: 18 V; time of treatment: 30 min.

consumption than Pt/Ti, together with higher efficiency (Fig. 8). The efficiency of Pt/Ti anode measured as the removed quantity of COD after 1 h of treatment time, under 1 A current and 1 m2 electrode surface, presents an optimal value after 20 min of treatment. In contrast, Nb/D show a very high efficiency during the first 10 min of treatment following continuous decrease during the treatment. The same behavior is presented for the energy consumption. This means that the "response" of the Nb/D anode, concerning the formation of oxidizing agents after the treatment is started, is much quicker than Pt/Ti anode.

Both anodes show great anodic stability and resistance to all kind of media such as acidic/basic or oxidative/reductive environment. After every treatment, both anodes require washing with tap water only. No permanent deactivation is observed during all the series of experiments performed for the present study.

In [Table 1,](#page-2-0) the main environmental parameters for both anodes, together with the initial values of the untreated wastewater is presented. The Nb/D anode achieves higher color removal on all three wavelengths.

The concentration of hypochlorite anions increases during the electrochemical treatment, while the concentration of chloride anions decreases. This means that a quantity of chlorides is oxidized, producing mainly hypochlorite anions, which speed up



Fig. 8. Anode efficiency and energy consumption during the treatment of real wastewater, using Nb/D and Pt/Ti as anodes. Applied potential: 18 V; time of treatment: 30 min.

the decoloration process. The quantity of hypochlorite anions is larger for Nb/D, justifying its high efficiency. Furthermore, the presence of low chloride concentration is adequate for fast and complete decoloration, thus requiring no further addition of electrolyte in the wastewater. The final pH is slightly alkaline at a value of about pH 8 using both Pt/Ti and Nb/D anodes.

Furthermore, there is a significant decrease in  $BOD<sub>5</sub>$  and COD for both anodes. However, the ratio COD/BOD5, which is a biodegradability indicator, is reduced only in the case of Nb/D proving that only Nb/D can provide a more biodegradable and less toxic final wastewater under the selected conditions.

Finally, TOC, the most important parameter, is also decreased significantly, although to a lower extent for both anodes indicating that the degradation proceeds further than azo-bond cleavage, but not as far as complete mineralization. The difference between COD and TOC values can be justified by the fact that many times  $K_2Cr_2O_7$  is not able to oxidize the whole amount of the organic matter during the determination of COD, thus resulting in reduced values. However, in all cases Nb/D exhibits better decoloration efficiency together with degradation to a higher extent than Pt/Ti. The fact that the COD/BOD<sub>5</sub> ratio is decreased for Nb/D indicates that the electrochemically treated wastewater could easily be completely mineralized under a subsequent biological treatment.

From a practical point of view, the most important achievement of the studied method is the quick and almost complete decoloration of the textile influent without using chemical additives, which are necessary for chemical treatment methods. Secondly, the method can be efficient under a wide range of pH in contrast to other treatment methods such as ozonation, biological and chemical methods. Thirdly, all parts of the instrumentation show great stability under redox, acidic or alkaline conditions, leading to long life efficiency of the method together with low fundamental costs. Fourthly, in case that Nb/D is used as an anode, the final wastewater is more degradable than the initial one regarding the COD/BOD<sub>5</sub> parameter. All the above benefits can be utilized in a pilot scale plant, which will result in a real scale pretreatment stage, prior to a main stage of biological treatment in order to estimate the economic feasibility of the method [\[31\].](#page-6-0)

# **4. Conclusions**

The newly developed electrochemical method seems to give rather satisfactory and very promising results.

Chloride and sulfate ions are mainly responsible for the indirect decoloration of the wastewater, while direct decoloration in the tested potential values  $(12-18 \text{ V})$  is almost absent.

The optimal pH range is acidic to moderate basic. Furthermore, no matter what the initial pH value is, the pH tends to reach a final value of  $pH 8$ , due to  $CO<sub>2</sub>$  and subsequent carbonate buffer formation, which indicates that mineralization proceeds at a remarkable rate.

Both Nb/D and Pt/Ti anodes exhibit great anodic stability and resistance to redox and acidic/basic environments, showing no deactivation. However, Nb/D achieves higher decoloration (up to 90%), together with higher anode efficiency and lower energy <span id="page-6-0"></span>consumption than Pt/Ti, with no further addition of electrolyte. The final wastewater is practically decolorized, containing very low concentrations of chlorides and the most harmful hypochlorites. For both anodes, no sludge formation is observed.

Nb/D achieves better environmental characteristics than Pt/Ti with 49.6%, 93.3% and 52.4% BOD<sub>5</sub>, COD and TOC removal, respectively. It is very important that  $\text{COD}/\text{BOD}_5$  is significantly reduced, indicating less toxic and more biodegradable wastewater, which can easily be completely mineralized by subsequent biological treatment. However, Nb/D a rather expensive material.

Extensive research has to be performed, aimed at the development of analytical methods for identification and determination of the final degradation products [24,32]. Such information is crucial for the monitoring of the treated wastewater and its characterization concerning its direct disposal to the environment or the subsequent treatment using specific biological method.

## **Acknowledgments**

This work has been funded by the Ministry of Development, General Secretariat of Research and Technology of Greece, within the frame of the YPER project. Additionally, we would like to thank TEXAPRET S.A. Dyeworks, Thessaloniki, Greece, for its co-operation and the supply of the azodyes.

#### **References**

- [1] O.J. Hao, H. Kim, P.H. Chiang, Crit. Rev. Environ. Sci. Tech. 30 (2000) 449–505.
- [2] Y.M. Slokar, A.M. Le Marechal, Dyes Pigments 37 (1998) 335–356.
- [3] A.T. Peters, H.S. Freeman, Analytical Chemistry of Synthetic Colorants, Blackie Academic & Professional, New York, 1995.
- [4] M.I. Beydilli, S.G. Pavlostathis, W.C. Tincher, Water Sci. Technol. 38 (1998) 225–232.
- [5] A. Kunz, H. Mansilla, N. Duran, Environ. Technol. 23 (2002) 911–918.
- [6] B.Y. Chen, Process Biochem. 38 (2002) 437–446.
- [7] L. Nicolet, U. Rott, Water Sci. Technol. 40 (1999) 191–198.
- [8] R. Ohura, A. Katayama, T. Takagishi, Textile Res. J. 62 (1992) 552–556.
- [9] I.M.C. Goncalves, A. Gomes, R. Bras, M.I.A. Ferra, M.T.P. Amorim, R.S. Porter, J. Soc. Dyers Colourists 116 (2000) 393–397.
- [10] J. Bell, J.J. Plumb, C.A. Buckley, D.C. Stuckey, J. Environ. Eng. ASCE 126 (2000) 1026–1032.
- [11] C. Palma, M.T. Moreira, I. Mielgo, G. Feijoo, J.M. Lema, Water Sci. Technol. 40 (1999) 131–136.
- [12] M. Perez, F. Torrades, X. Domenech, J. Peral, Water Res. 36 (2002) 2703–2710.
- [13] P.K. Wonk, P.Y. Yuen, Water Res. 30 (1996) 1736–1744.
- [14] L. Szpyrkowicz, C. Juzzolino, S.N. Kaul, Water Res. 35 (2001) 2129–2136.
- [15] J. Wu, M.A. Eiteman, S.E. Law, J. Environ. Eng. ASCE 124 (1998) 272–277.
- [16] M.F. Sevimli, H.Z. Sarikaya, J. Chem. Technol. Biotechnol. 77 (2002) 842–850.
- [17] J. Sarasa, M.P. Roche, M.P. Ormad, E. Gimeno, A. Puig, J.L. Ovelleiro, Water Res. 32 (1998) 2721–2727.
- [18] S.H. Lin, C.M. Lin, Water Res. 27 (1993) 1743–1748.
- [19] K. Tanaka, K. Padermpole, T. Hisanaga, Water Res. 34 (2000) 327–333.
- [20] S.H. Lin, C.F. Peng, Water Res. 30 (1996) 587–592.
- [21] X.M. Zhan, J.L. Wang, X.H. Wen, Y. Qian, Environ. Technol. 22 (2001) 1105–1111.
- [22] N. Mohan, N. Balasubramanian, V. Subramanian, Chem. Eng. Technol. 24 (2001) 749–753.
- [23] A.G. Vlyssides, D. Papaioannou, M. Loizidou, P.K. Karlis, A.A. Zorpas, Waste Manage. 20 (2000) 569–574.
- [24] A. Gonzalez, A.A. Pelaez-Cid, J. Chromatogr. A 889 (2000) 253– 259.
- [25] M.C. Gutierrez, M. Crespi, J. Soc. Dyers Colourists 115 (1999) 342– 345.
- [26] J. Naumczyk, L. Szpyrkowicz, F. ZilioGrandi, Water Sci. Technol. 34 (1996) 17–24.
- [27] A.G. Vlyssides, M. Loisidou, P.K. Karlis, A.A. Zorbas, D. Papaioannou, J. Hazardous Mater. B 70 (1999) 41–52.
- [28] D. Pletcher, F.C. Walsh, Industrial Electrochemistry, 2nd ed., Chapman and Hall, New York, 1990, pp. 353.
- [29] D. Rajkumar, B.J. Song, J.G. Kim, Dyes Pigments 71 (2006) 244–250.
- [30] L. Szpyrkowicz, C. Juzzolino, S.N. Kaul, S. Daniele, M.D. de Faveri, Ind. Eng. Chem. Res. 39 (2000) 3241–3248.
- [31] A. Sakalis, K. Mpoulmpasakos, U. Nickel, K. Fytianos, A. Voulgaropoulos, Chem. Eng. J 111 (2005) 63–70.
- [32] A. Sakalis, D. Ansorgová, M. Holčapek, P. Jandera, A. Voulgaropoulos, Int. J. Environ. Anal. Chem. 84 (2004) 875–888.
- [33] I. Tröster, L. Schäfer, M. Fryda, New diamond front, Carbon Technol. 12 (2002) 89.
- [34] S.I. Agadzhanyan, R.G. Romanova, G.V. Korshin, P.A. Kirpichnikov, Russian J. Appl. Chem. 69 (1996) 380–384.
- [35] E.A. Ananeva, G.L. Vidovich, M.D. Krotova, G.A. Bogdanovskii, Russian J. Electrochem. 32 (1996) 936–938.
- [36] APHA, AWWA-WPCF, Standard Methods for the Examination of Water and Wastewater, American Public Health Association, Washington, 1995, pp. 21–60.