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Evaluation of a novel electrochemical pilot plant process for azodyes removal from textile wastewater

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Abstract

A novel pilot plant for the electrochemical treatment of textile wastewater is discussed in this paper. The process is based on the electrolytic degradation of azodyes, applying a specific potential with on line measurement of current, pH and temperature. Batch experiments are performed for single electrolytic cell and continuous flow experiments for serial electrolytic cell apparatus (cascade system), using both synthetic and real wastewater samples. For synthetic samples treatment, four commercially pure azodyes (Reactive Orange 91, Reactive Red 184, Reactive Blue 182 and Reactive Black 5) are used, while sodium chloride (NaCl) and sodium sulfate (Na_2SO_4) are tested as supporting electrolytes. Real wastewater treatment under optimal conditions yield 94.4% dye removal and neutral final pH. Biologically Oxygen Demand measured after 5 days (BOD_5) and Chemically Oxygen Demand (COD) values are reduced by 35 and 45%, respectively, while COD/BOD_5 ratio is reduced from 4.3 to 3.6 final value. The proposed pilot plant achieves almost complete decoloration requiring no further addition of electrolyte or any other chemical agent. Thus, it could easily be used as a pretreatment stage prior to biological treatment.

Keywords: Electrochemical treatment; Pilot plant; Degradation; Decoloration

1. Introduction

Textile industry provides huge quantities of wastewater as a result of many intermediate stages using water [1]. Moreover, each intermediate stage provides different wastewater, so the final wastewater can be considered as a mixture of intermediate wastewater, containing mainly unfixed dyes as well as other impurities such as, polyvinyl alcohol, starches, surfactants, pesticides, biocides and relatively high salinity [2].

However, the increased color intensity is the most serious problem of the wastewater provided by the Textile Industries not only because of aesthetical displeasure, but also because many of the commercial azodyes can produce hazardous aromatic amines, as well as other highly toxic by-products through metabolic processes in plants and animals or directly after the disposal in lakes, rivers or sea [3–6].

Concerning the reactive dyes which are mainly used for textile dying processes, it is known that 30% of the initial amount of the dye is released in the wastewater due to hydrolysis side reaction, resulting in limited degree of fixation [7]. Moreover, azodyes which are synthetic products, show rather low biodegradability, firstly because of lack of natural biodegradation paths and secondly because of stereochemical interferences concerning the accession of the reductant or oxidant molecule to the azo-group [8,9]. As a result, traditional biological processes are not able to fully decolorize azodye wastewater [10–15].

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Other conventional methods such as physical [16], chemical [17] and photocatalytic processes [18–20] have individual advantages, but also have constraints causing inadequate effectiveness, if applied individually [1].

For example, adsorption on activated carbon is only successful for hydrophobic dyes, coagulation is partially effective for highly soluble dyes and Fenton's reagent is effective at pH < 3.5 [21–22], while ozonation is effective at high pH values [23].

Furthermore, ozonation can result in colorless wastewater. However, hazardous organic material is slightly reduced, causing high final total organic carbon (TOC) and COD values, together with high operational cost [24–26].

Electrochemical treatment is a relatively new technique providing certain advantages such as almost complete decoloration, operation under moderate pH range, low final temperature, significant COD and BOD_5 reduction as well as no sludge formation [15,27–31]. However, in most cases [29] high concentrations of supporting electrolytes, especially NaCl, are required for satisfactory results leading to high concentrations of hypochlorite anions, free chlorine and polychlorinated aromatic products, which are extremely harmful for the environment [1,32–36]. Therefore, novel electrochemical processes requiring no further electrolyte addition, are essential for environmentally friendly application of this technique.

Elsewhere a combination of fluidized biofilm process with chemical coagulation and electrochemical oxidation is proposed, without however avoiding sludge formation [39].

In this paper, a pilot plant electrochemical process is proposed achieving almost complete decoloration and satisfactory COD and BOD_5 reduction requiring no further addition of supporting electrolyte. The whole process is based on a previous work of our group [37,38] and is about to operate as a pre-treatment stage prior to biological treatment, regarding that combined processes are the most hopeful solution for complete mineralization of textile wastewater and safe disposal to the environment [39,40], since color limits of textile wastewater are rather strict all over world [41–45]. For this purpose, batch experiments are performed evaluating the efficiency of the electrolytic cell. Four commercial azodyes (C.I names, Reactive Orange 91, Reactive Red 184, Reactive Blue 182 and Reactive Black 5) are treated using NaCl and Na_2SO_4 as supporting electrolytes, while real wastewater samples, without any addition of supporting electrolyte, are treated under batch and continuous flow experiments using a cascade system. In all cases a constant potential is applied and specially treated carbon fleece is used as cathode, while titanium coated with platinum film (Pt/Ti) is used as anode. Parameters such as temperature, cell current and pH are checked on line, while BOD_5, COD and COD/BOD_5 values are determined in case of real wastewater samples. Color removal is measured in all cases and experimental data for energy consumption and anode efficiency is presented.

Table 1
Environmental parameters of initial wastewater

Environmental parameter	Initial wastewater
Total suspended solids (g/dm^3)	0.020
pH	8–9
Color, λ_{max} = 525 nm (absorption units)	0.182
Chlorides (g/dm^3)	0.224
BOD_5 (g/dm^3)	0.142
COD (g/dm^3)	0.608
Total organic carbon (g/dm^3)	0.164

2. Materials and methods

2.1. Reagents

All dyes 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). NaCl and Na_2SO_4 used as electrolytes as well as reagents used for BOD and COD 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 the real wastewater. Doubly distilled water is used for all measurements. The real wastewater was obtained from the co-operating company (Texapret SA, Thessaloniki, Greece) and its initial characteristics are shown in Table 1. All parameters are measured according to standard methods for examination of water and wastewater [46].

2.2. Electrodes

Carbon fleece used as cathode is Sigatherm PR201-16 model, obtained from SGL Carbon Group (Germany). It is a specially treated and modified carbon, achieving large porosity and active surface. Additionally, this type of electrode shows great stability, acid, base and redox resistance, practically no deactivation through long term use and is easily cleaned and stored.

The anode made of titanium substrate coated with platinum film (50 g Pt/m^2), is obtained from Metakem GmbH (Germany), and shows excellent effectiveness and stability as well as easy cleaning and storage.

2.3. Electrolytic cell—cascade system

The pilot plant electrolytic cell as well as the cascade system is manufactured by the cooperating Institute of Physical Chemistry, University of Erlangen (Germany).

The capacity of the electrolytic cell is 50 dm^3. The cell and the electrodes can be seen in Fig. 1.

The inner coat is made of Plexiglas and the outer coat is made of stainless steel. The aeration of each cell is provided by a perforated plate made of Plexiglas and placed at

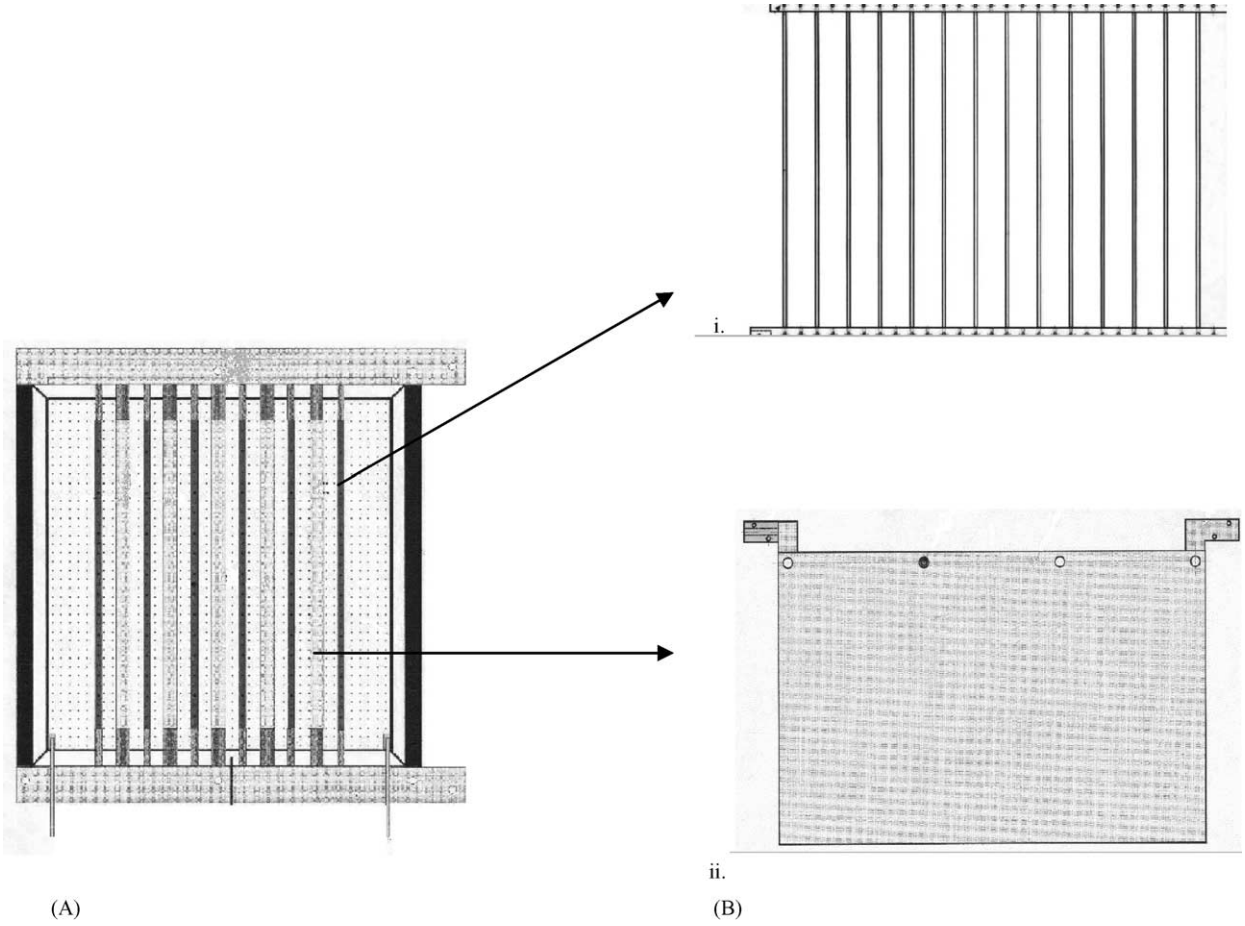

Fig. 1. (A) Ground plan of the pilot plant electrochemical cell and (B) i: the Pt/Ti anode and ii: the carbon fleece cathode.

the bottom of the cell. A compact air pump (oil free model, ~300 $dm^3\ min^{-1}$) is used for air supply.

Five cathode plates and six anodes of 15 Pt/Ti parallel cylindrical wires adapted on stainless steel frames are sequentially settled on suitable copper substrates which are adapted on the cell and connected via cables parallelly with two pairs of batteries providing 12 V potential. The distance between the electrodes is adjustable and anodes are electrically isolated from the copper substrate of the cathodes by suitable Teflon isolators and vice versa. All geometrical data for the electrodes are presented in Table 2.

The cascade system is basically consisted of a main wastewater tank with 1000 dm^3 capacity, a smaller tank (40 dm^3) for volume adjustment and three parallel electrolytic cells placed in different height.

The main wastewater tank is made of Plexiglas and the initial wastewater has a constant suitable temperature obtained through heat exchanger. The power supply is provided by two parallely connected pairs of batteries per electrolytic cell (12 V, 200 A dc, 2.4 kW) and compact air pumps are used for air supply. An underwater pump (flow rate: 2–10 $dm^3\ min^{-1}$) is used for the adjustment of the continuous flow of the wastewater from the main tank to the electrolytic cells, while hydrostatic pressure ensures the flow through the electrolytic cells due to different height of each cell. A recycling loop is used in order to keep constant the height of the wastewa-

Table 2
Dimensions of electrodes

	Each electrode	Electrolytic cell (five cathodes–six anodes)	Cascade system (three electrolytic cells)
Dimension of cathode (m)	0.280 × 0.440	5 × 0.280 × 0.440	3 × 5 × 0.280 × 0.440
Cathode surface (m^2)	0.120	0.120	0.120
Cathode total surface (m^2)	0.240	1.2	3.6
Dimension of anode (m)	15 × 0.003[a] × 0.340	15 × 0.003[a] × 0.340	15 × 0.003[a] × 0.340
Anode surface (m^2)	0.048	0.048	0.048
Anode total surface (m^2)	0.048	0.29	0.864

[a] Diameter of each anode wire.

ter in the adjustment tank ensuring the constant hydrostatic pressure between the adjustment tank and the electrolytic cell circuit, thus providing constant flow through the cells.

2.4. Experimental procedure

Initially, batch experiments are performed in a single electrolytic cell, with synthetic wastewater samples containing 5×10^{-4} M azodye diluted in tap water as well as specific concentration of supporting electrolyte. Regarding the electrolyte concentration, the short time of treatment, the possibility of the electrode deactivation and the overheat of the effluent [37], the optimal potential value is 12 V. This potential value provides total current of approximately 130 A and the wastewater is treated for a specific period of time. Sampling is performed every 20 min, since shorter time of sampling drives to usual and expected data as demonstrated in previous work [37]. UV–vis spectra of each sample are recorded using a Jasco V-530 spectrophotometer (Japan) with 10^{-2} m path length cells. Additionally, temperature, pH (Consort C830, Belgium) and current (ECT-689 clamp-on multimeter, Schmidt Scientific Taiwan Ltd.) are measured on line.

In a second stage, batch experiments of real wastewater are performed using also single electrolytic cell. Besides all the above-mentioned parameters, BOD_5, COD and COD/BOD_5 values are also measured for every sample in each experiment, while data for the energy consumption and the anode efficiency are presented.

Finally continuous flow experiments are performed testing the pilot plant cascade system. The decoloration process starts under batch conditions, till constant UV–vis absorption, approximately after 30 min of treatment, when the continuous flow process starts. A flow rate of 6 dm^3 min^{-1} is chosen as optimal value and sampling from all cells is performed every 10 min for the batch process and every 15 min for the continuous flow process. Decoloration process, current and temperature are monitored in each of the three cells.

3. Results and discussion

3.1. Batch experiments

Experiments using synthetic wastewater samples are initially performed in order to clarify the influence of the nature of the electrolyte on the efficiency of the method. In Fig. 2 the decoloration progress using either NaCl or Na_2SO_4 for all azodyes is presented.

It is obvious that NaCl causes quicker and more complete decoloration than Na_2SO_4 for all dyes. Especially for Reactive Blue 182 after 100 min of treatment, 99% of the initial color is removed from the wastewater, while for Reactive Red 184, more than 99.5% of the color is removed after 120 min of treatment. This rapid decoloration indicates that initial dyes are fully degraded, giving smaller and colorless organic or

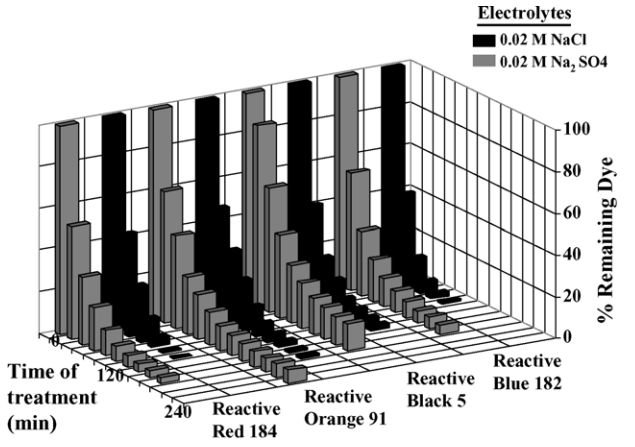

Fig. 2. The % color removal during the treatment of synthetic azodye samples using either 0.02 M NaCl or 0.02 M Na_2SO_4 as supporting electrolytes. Concentration of each azodye: 5×10^{-4} M. Applied potential: 12 V. Distance between electrodes: 3 cm. Measured wavelength: Reactive Orange 91: 416 nm, Reactive Blue 182: 612 nm, Reactive Black 5: 590 nm, Reactive Red 184: 540 nm.

inorganic products, which can further be biologically treated for complete mineralization of the wastewater. The complete absence of the initial dye, together with the presence of some organic and inorganic products, is proved by extensive research for the identification of the final degradation products of the treated wastewater using suitable hyphenated analytical techniques such as Liquid Chromatography–Mass Spectrometry (LC/MS) [38]. It is well known that the electrolysis of NaCl results in some very strong oxidants, such as free chlorine (Cl_2) and hypochlorite anions (ClO^-) [29,47,48,49]. On the contrary, Na_2SO_4 electrolysis drives mainly to the formation of SO_2 especially in acidic media, which is just a moderate reductant. The whole decoloration proceeds mainly via direct redox reactions on the electrodes, enhanced by indirect redox reactions by the produced oxidants or reductants. The stronger the oxidants or reductants are, the better enhancement they can achieve. Consequently, the dye molecule can more easily be degraded in aquatic media containing chloride anions (Cl^-). Additionally, each dye shows different degradeability for both electrolytes due to stereochemical and resonance inductive effects. However, the final degradation especially using NaCl is rather satisfactory.

Concerning the current and temperature values during the decoloration process, both show smaller increase in case that NaCl is used as electrolyte (Fig. 3). This means that treatment under Na_2SO_4, produces more ionic products, increasing the ionic strength of the wastewater. It is known that almost all azodyes (including those used in this work) are polysulphonated compounds in order to be water-soluble. In our previous work [38], significant quantities of $HOSO_3^-$ were identified in the final wastewater, as a result of the degradation of the dye molecules. These anions together with other ionic degradation products cause the increase of the current. In the case of NaCl, the increase is smaller probably because many of the ionic products are rapidly further degraded in non-ionic

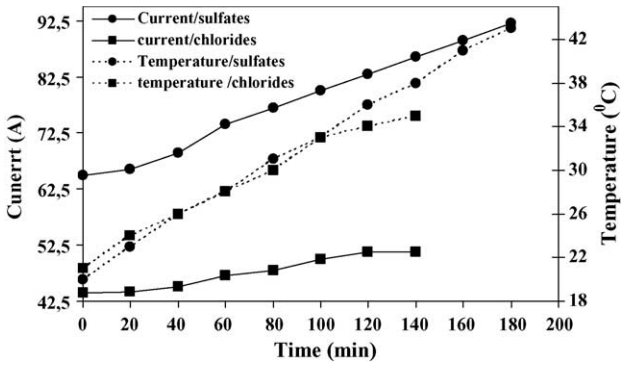

Fig. 3. Diagrams of temperature and current, during the electrochemical treatment of 5×10^{-4} M Reactive Black 5 synthetic sample, using either 0.02 M NaCl or 0.02 M Na_2SO_4 as supporting electrolytes. Applied potential: 12 V. Distance between electrodes: 3 cm. Measured wavelength: 590 nm.

final products (N_2, CO_2, SO_2/SO_3). Final wastewater with as low ionic strength as possible is basic demand for both high biodegradability and safe disposal in the environment.

In dye baths, NaCl is the main salt used for the optimal fixation of the dyes on the textile substrate. Therefore, the real wastewater contains the required quantity of NaCl to carry out the electrochemical treatment, without any further addition of electrolyte, which would increase the ionic strength.

In Fig. 4, the spectra of real wastewater treatment samples are presented.

It is shown that after 75 min of treatment there is almost complete decoloration. This means that the concentration of salts contained already in the wastewater is adequate for fast and complete color removal. It is significant that just after 15 min, the decoloration is almost completed.

The anode efficiency during the treatment, measured in kg COD h^{-1} m^{-2} A^{-1}, is optimal around 45 min of treatment as seen in Fig. 5a. After 45 min the anode efficiency is decreased mainly due to the significant decrease of the Cl^- which are oxidized during the treatment. As a result, the formation of strong oxidants which enhance the decoloration and degradation process is also reduced.

As can be seen in Fig. 5b, the energy consumption, which is measured in kW h kg^{-1} COD, is reduced during the first 45 min of the treatment. This means that less energy is needed

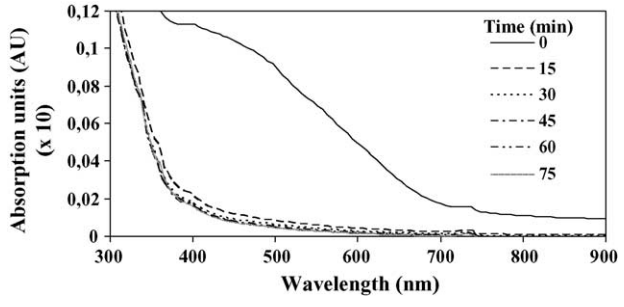

Fig. 4. The UV–vis spectra of real wastewater sample during the electrochemical treatment. Applied potential: 12 V. Distance between electrodes: 3 cm.

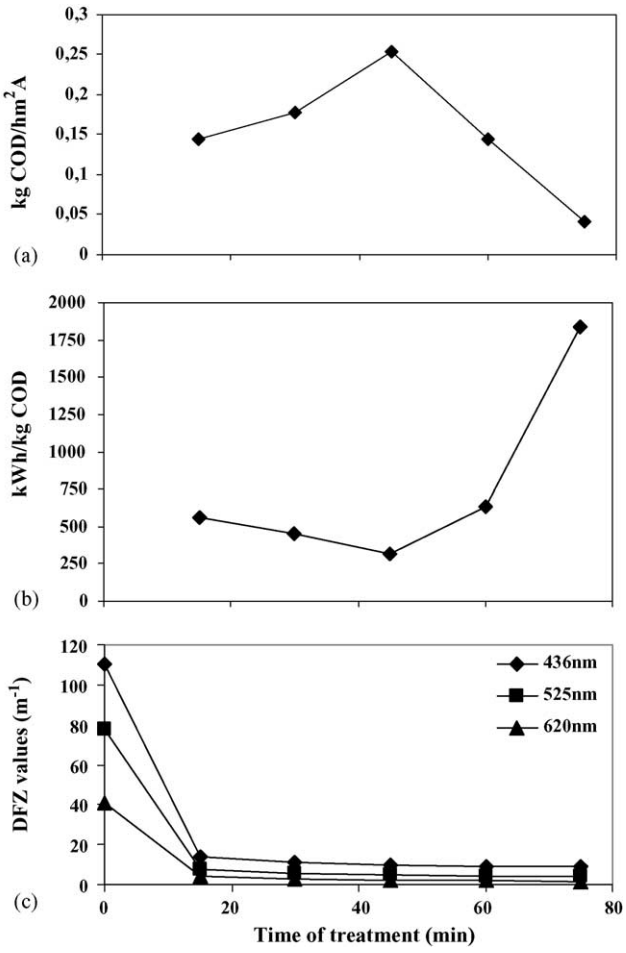

Fig. 5. (a) Anode efficiency during the decoloration process. Applied potential: 12 V. Distance between electrodes: 3 cm. (b) Energy consumption during the decoloration process. Applied potential: 12 V. Distance between electrodes: 3 cm. (c) DFZ values (DFZ = $A(1000)/d$, A = absorbance, d = cell length in mm) for 436 nm (yellow), 525 nm (red) and 620 nm (blue), during the electrochemical treatment for the real wastewater sample. Applied potential: 12 V. Distance between electrodes: 3 cm. Measured wavelengths: 436, 525 and 620 nm.

for the removal of 1 kg of COD, so the treatment proceeds efficiently and with low energy demand. After 45 min of treatment the energy consumption is increased rapidly, so the whole treatment loses its efficiency and becomes energy consuming. Therefore, 50 min of treatment are enough for the complete treatment of the wastewater and from the economic point of view, they are chosen as the optimal period of treatment.

The whole decoloration process can be seen in Table 3, where crucial environmental parameters are measured.

The initial pH is decreased approaching pH 7. This is very important because finally treated wastewater should be neutral prior any disposal. Furthermore, BOD_5 and COD are decreased up to 36 and 45%, respectively, while COD/BOD_5 ratio is decreased from 4.3 to 3.7, indicating that the final wastewater is much more biodegradable than the initial one. Additionally, the decrease of COD and BOD_5 means that not

Table 3
Profiles of the main environmental parameters during the real wastewater batch treatment

Time of treatment (min)	pH	COD (g/dm^3)	BOD_5 (g/dm^3)	COD/BOD_5	Remained color (%) (λ = 525nm)	Temperature (°C)
0	10.2	0.608	0.142	4.3	100	26
15	9.5	0.560	0.137	4.1	9.6	25
30	9.2	0.496	0.110	4.5	7.1	30
45	8.8	0.400	0.097	4.1	6.0	45
60	8.5	0.352	0.096	3.7	5.1	60
75	8.4	0.336	0.091	3.7	5.0	75

only decoloration takes place during the treatment, but also further degradation of the initial colorless products. This is the main task of the electrochemical process in order to create a more degradable wastewater for further biological treatment. Concerning the color removal, there is a decrease up to 95% after 75 min of treatment. Additionally, after only 15 min of treatment almost 90% of the initial color was removed. Practically, the final wastewater is colorless and much more biodegradable than the initial one.

In Fig. 5c, DFZ values of real wastewater sample are plotted versus time of treatment. These values are used by Germany as the official system for the color measurement and are depended on Beer's law. So, DFZ = $A(1000)/d$, where A is the color absorption and d the distance of the used UV–vis cell in mm. After 75 min of treatment DFZ value at 436 nm is 8.9, at 525 nm is 3.9 and at 620 is 1.5. Besides 436 nm, the DFZ values at 525 and 620 nm in final wastewater are below German standards (7, 5 and 3 m^{-1} DFZ values). This means that the concentration of salts contained already in the wastewater is adequate for fast and complete dye removal.

3.2. Continuous flow experiments

Batch conditions are initially applied in order to stabilize the wastewater in the electrolytic cells. Since color removal is constant in all three cells, the flow rate is gradually increased up to 6 dm^3 min^{-1}. This flow rate is chosen as the optimal value for the continuous flow procedure, following the criteria that decoloration over 90% should be achieved in the shortest possible time. In Fig. 6a the decoloration process measured at 525 nm is presented for both conditions.

Under batch treatment, the percentage of the color removal is increased up to 90% after 30 min in all three cells. Subsequently, the flow rate is increased up to 6 dm^3 min^{-1} resulting in rapid increase of the remaining color mainly in the first electrolytic cell. In approximately 10 min, the color removal in all cells is stabilized and in the third cell it is around 10% of the initial amount, thus practically after 40 min of treatment, the effluent from the third cell can be driven to the biological treatment. Under continuous flow conditions, an amount of 50 dm^3 wastewater needs around 30 min of treatment in the three cells before the subsequent biological process.

The temperature profile for the three cells is presented in Fig. 6b. In all cells the final temperature does not exceed 38 °C. After 30 min of treatment (continuous flow is applied),

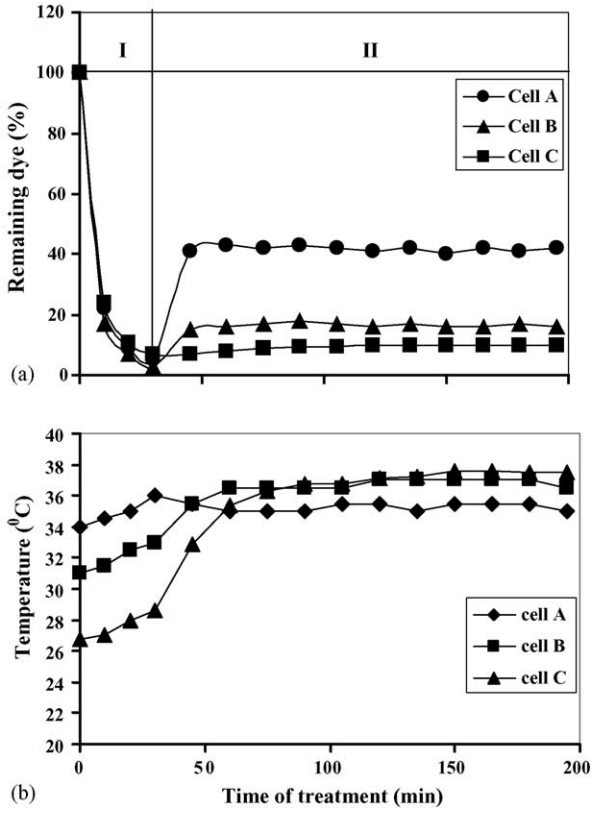

Fig. 6. (a) The % remaining color during the decoloration process using real wastewater sample treated in the cascade system. (I) batch condition. (II) continuous flow condition, flow rate: 6 dm^3 min^{-1}. Applied potential: 12 V. Distance between electrodes: 3 cm. Measured wavelength: 525 nm. (b) The temperature profile for the three cells, during the real wastewater cascade system treatment. Applied potential: 12 V. Distance between electrodes: 3 cm.

the temperature is not further increased and it is stabilized at low values. Compared with the batch experiment (Fig. 3) the final temperature is significantly lower, because of the wastewater flow, which decreases considerably the final temperature, thus providing suitable final wastewater for environmental disposal or further biological treatment.

4. Conclusions

A novel pilot plant electrochemical method is evaluated in this study. Initial batch experiments using synthetic wastewa-

ter samples showed that both NaCl and Na_2SO_4, enhance the decoloration process, though NaCl showed better behavior. Since both these electrolytes exist in the textile wastewater as remaining dye-bath additives, experiments with real samples were run without further addition of any chemical reagent, giving similar or lower DFZ values than German standards. Furthermore, pH during the treatment is reduced to almost neutral values, while COD and BOD_5 are reduced up to 45 and 36%, respectively with COD/BOD_5 decrease from 4.3 to 3.7 final value, indicating that the final wastewater is more biodegradable and less toxic, thus it is suitable for effective and complete further biological treatment. From the economic point of view, data for anode efficiency and energy consumption showed an optimal time of treatment approximately 45 min. Finally, continuous flow experiments, using the cascade system, resulted in final effluent with only 10% of the initial dye content after 40 min of treatment, while final temperature is 38 °C. In conclusion, the application of the proposed method on textile wastewater results in almost colorless final wastewater having considerably reduced values of COD, BOD_5, COD/BOD_5, as well as appropriate temperature and pH to render it suitable for successive further biological treatment.

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References

[1] O.J. Hao, H. Kim, P.C. Chiang, Decolorization of wastewater, Crit. Rev. Environ. Sci. Technol. 30 (4) (2000) 449–505.
[2] A. Uygur, An overview of oxidative and photooxidative decolorisation treatments of textile waste waters, J. Soc. Dyers Colour. 113 (7/8) (1997) 211–217.
[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, Decolorization and toxicity screening of selected reactive azo dyes under methanogenic conditions, Water Sci. Technol. 38 (4–5) (1998) 225–232.
[5] A. Kunz, H. Mansilla, N. Duran, A degradation and toxicity study of three textile reactive dyes by ozone, Environ. Technol. 23 (8) (2002) 911–918.
[6] B.Y. Chen, Understanding decolorization characteristics of reactive azo dyes by *Pseudomonas luteola*: toxicity and kinetics, Process. Biochem. 38 (3) (2002) 437–446.
[7] T. Bechtold, E. Burtscher, A. Turcanu, Cathodic decolourisation of textile waste water containing reactive dyes using a multi-cathode electrolyser, J. Chem. Technol. Biot. 76 (2001) 303–311.
[8] U. Pagga, D. Brown, The degradation of dyestuffs.-II. Behavior of dyestuffs in aerobic biodegradation tests, Chemosphere 15 (4) (1986) 479–491.
[9] Y.M. Slokar, A.M. Marechal, Methods of decoloration of textile wastewaters, Dyes Pigments 37 (4) (1997) 335–356.
[10] L. Young, Y. Jian, Ligninase-catalyzed decolorization of synthetic dyes, Water Res. 31 (5) (1997) 1187–1193.
[11] E. Razo-Flores, M. Luijten, B. Donlon, G. Lettinga, J. Field, Biodegradation of selected azo dyes under methanogenic conditions, Water Sci. Technol. 36 (6–7) (1997) 65–72.
[12] V.V. Konovalova, M.T. Bryk, R.R. Nigmatullin, P.I. Gvozdyak, O.F. Udilova, Biocatalytic membranes for ultrafiltration treatment of wastewater containing dyes, Bioprocess. Eng. 23 (6) (2000) 651–656.
[13] I.M.C. Goncalves, A. Gomes, R. Bras, M.I.A. Ferra, M.T.P. Amorim, R.S. Porter, Biological treatment of effluent containing textile dyes, J. Soc. Dyers Colour. 116 (12) (2000) 393–397.
[14] J. Bell, J.J. Plumb, C.A. Buckley, D.C. Stuckey, Treatment and decolorization of dyes in an anaerobic baffled reactor, J. Environ. Eng.-ASCE 126 (11) (2000) 1026–1032.
[15] S.V. Mohan, N.C. Rao, K.K. Prasad, J. Karthikeyan, Treatment of simulated Reactive Yellow 22 (Azo) dye effluents using *Spirogyra* species, Waste Manage. 22 (6) (2002) 575–582.
[16] L. Nicolet, U. Rott, Recirculation of powdered activated carbon for the adsorption of dyes in municipal wastewater treatment plants, Water Sci. Technol. 40 (1) (1999) 191–198.
[17] R. Ohura, A. Katayama, T. Takagishi, Degradation of sulfonated azo dyes with sodium percarbonate, Text. Res. J. 62 (9) (1992) 552–556.
[18] M.S.T. Goncalves, A.M.F. Oliveira-Campos, E.M.M.S. Pinto, P.M.S. Plasencia, M.J.R.P. Queiroz, Photochemical treatment of solutions of azo dyes containing TiO_2, Chemosphere 39 (5) (1999) 781–786.
[19] J.L. Hong, M. Otaki, J.D. Rouse, K. Furukawa, Continuous treatment of azo acid dyes by photo-dependent denitrifying sludge, J. Environ. Sci.—China 14 (3) (2002) 296–302.
[20] K. Tanaka, K. Padermpole, T. Hisanaga, Photocatalytic degradation of commercial azodyes, Water Res. 34 (1) (2000) 327–333.
[21] W.G. Kuo, Decolorizing dye wastewater with Fenton's reagent, Water Res. 26 (7) (1992) 881–886.
[22] E.G. Solozhenko, N.M. Soboleva, V.V. Goncharuk, Decolourization of azodye solutions by Fenton's oxidation, Water Res. 29 (9) (1995) 2206–2210.
[23] J. Wu, M.A. Eiteman, S.E. Law, Evaluation of membrane filtration and ozonation processes for treatment of reactive-dye wastewater, J. Environ. Eng.-ASCE 124 (3) (1998) 272–277.
[24] S.H. Lin, C.M. Lin, Treatment of textile waste effluent by ozonation and chemical coagulation, Water Res. 27 (12) (1993) 1743–1748.
[25] M.F. Sevimli, H.Z. Sarikaya, Ozone treatment of textile effluents and dyes: effect of applied ozone dose, pH and dye concentration, J. Chem. Technol. Biot. 77 (7) (2002) 842–850.
[26] J. Sarasa, M.P. Roche, M.P. Ormad, E. Gimeno, A. Puig, J.L. Ovelleiro, Treatment of a wastewater resulting from dyes manufacturing with ozone and chemical coagulation, Water Res. 32 (9) (1998) 2721–2727.
[27] J.-S. Do, M.-L. Chen, Decolorization of dye-containing solutions by electrocoagulaton, J. Appl. Electrochem. 24 (8) (1994) 785–790.
[28] M.C. Gutierrez, M. Crespi, A review of electrochemical treatments for colour elimination, J. Soc. Dyers Colour. 115 (11) (1999) 342–345.
[29] A.G. Vlyssides, M. Loisidou, P.K. Karlis, A.A. Zorbas, D. Papaioannou, Electrochemical treatment of a textile dye wastewater using Pt/Ti electrode, J. Hazard. Mater. B70 (1999) 41–52.
[30] J.P. Lorimer, T.J. Manson, M. Plates, S.S. Phull, Dye effluent decolourisation using ultrasonically assisted electro-oxidation, Ultrason. Sonochem. 7 (4) (2000) 237–242.
[31] X.M. Zhan, J.L. Wang, X.H. Wen, Y. Qian, Indirect electrochemical treatment of saline dyestuff wastewater, Environ. Technol. 22 (9) (2001) 1105–1111.
[32] J. Naumczyk, L. Szpyrkowicz, F. Zilio-Grandi, Electrochemical treatment of textile wastewater, Water Sci. Technol. 34 (11) (1996) 17–24.
[33] A. Gonzalez, A.A. Pelaez-Cid, Electrochemical treatment of textile dyes and their analysis by high-performance liquid chromatography with diode array detection, J. Chromatogr. A 889 (1–2) (2002) 253–259.

[34] W. Feng, D. Nansheng, H. Helin, Degradation mechanism of azo dye C. I. Reactive red 2 by iron powder reduction and photooxidation in aqueous solutions, Chemosphere 41 (8) (2000) 1233–1238.
[35] M. Holčapek, P. Jandera, P. Zderadička, High performance liquid chromatography–mass spectrometric analysis of sulphonated dyes and intermediates, J. Chromatogr. A 926 (2001) 175–186.
[36] A. Rehorek, K. Urbig, R. Meurer, C. Schäfer, A. Plum, G. Braun, Monitoring of azo dye degradation processes in a bioreactor by on-line high-performance liquid chromatography, J. Chromatogr. A 949 (2002) 263–268.
[37] A. Sakalis, A. Voulgaropoulos, P. Jandera, D. Ansorgova, M. Holcapek, Separation, determination and Identification of initial azodyes and final degradation products in electrochemically treated synthetic azodyes aqueous solutions, in: F. Adams, E. Rosenberg, L. Van't dack (Eds.), Proceedings of the Sixth Euroconference of Environmental Analytical Chemistry, Centerparcs Erperheide, Peer, Belgium, 2002, p. 58.
[38] A. Sakalis, D. Ansorgova, M. Holcapek, P. Jandera, A. Voulgaropoulos, Analysis of sulphonated azodyes and their degradation products in aqueous solutions treated with a new electrochemical method, Int. J. Environ. Anal. Chem. 84 (11) (2004) 875–888.
[39] K. Tak-Hyun, P. Chulhwan, L. Jinwon, S. Eung-Bai, K. Sangyong, Pilot scale treatment of textile wastewater by combined process (fluidized biofilm process–chemical coagulation–electrochemical oxidation), Water Res. 36 (2002) 3979–3988.
[40] L.N. Nelson, D.L. Avijit, Industrial and Hazardous Waste Treatment, Van Nostrand Reinhold, New York, 1991.
[41] EPA. Textile Mill Point Source Category Effluent Limitation Guidelines, Pretreatment Standards and New Source Performance Standards, 61/204/62-241, US Environmental Protection Agency, Cincinnati, OH, 1979.
[42] F. Gahr, F. Hermanutz, W. Oppermann, Ozonation-An important technique to comply with the new German laws for textile wastewater treatment, Water Sci. Technol. 30 (3) (1994) 255–263.
[43] J.H. Churchley, Removal of dyewaste color from sewage effluent-the use of a full scale ozone plant, Water Sci. Technol. 30 (3) (1994) 275–284.
[44] C.-N. Chang, R.-F. Yu, A.C. Chao, S. Tojo, On-line monitoring and control of the textile wastewater color removal process, Water Sci. Technol. 30 (3) (1994) 265–274.
[45] A. Rozzi, F. Malpei, L. Bonomo, R. Bianchi, Textile wastewater reuse in Northern Italy, Water Sci. Technol. 39 (5) (1999) 122–128.
[46] APHA, Standard Methods for Examination of Water and Wastewater, 19th ed., American Public Health Association, Washington, DC, 1995.
[47] D. Pletcher, F.C. Walsh, Industrial Electrochemistry, 2nd ed., Chapman and Hall, New York, 1990, pp. 353–357.
[48] S.I. Agadzhanyan, R.G. Romanova, G.V. Korshin, P.A. Kirpichnikov, Physicochemical properties of sodium chloride solutions after electrochemical treatment in a flow electrolyzer, Russ. J. Appl. Chem. 69 (3) (1996) 380–384.
[49] E.A. Ananeva, G.L. Vidovich, M.D. Krotova, G.A. Bogdanovskii, The study of a photochemical and electrochemical treatment of aqueous solutions of azo dyes, Russ. J. Electrochem. 32 (8) (1996) 936–938.