Chemical Engineering Journal 148 (2009) 444–451

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Electrochemical treatment of simulated industrial paint wastewater in a continuous tubular reactor

Bahadır K. Körbahti[a], Abdurrahman Tanyolaç[b,*]

[a] Faculty of Engineering, Department of Chemical Engineering, University of Mersin, Çiftlikköy 33343, Mersin, Turkey
[b] Faculty of Engineering, Department of Chemical Engineering, Hacettepe University, Beytepe Campus, Beytepe 06800, Ankara, Turkey

ARTICLE INFO

Article history:
Received 21 June 2008
Received in revised form 5 September 2008
Accepted 17 September 2008

Keywords:
D-optimal design
Electrochemical wastewater treatment
Energy consumption
Mass transfer
Optimization
Paint wastewater
Tubular reactor

ABSTRACT

The electrochemical treatment of industrial water-based paint wastewater was investigated in a continuous tubular reactor constructed from a stainless steel tube with a cylindrical carbon anode. Industrial wastewater was prepared by thinning a commercial paint down to 4.4% (w/v) with water, which is the solid material content of the wastewater generated in the paint manufacture. The effects of residence time on chemical oxygen demand (COD), color and turbidity removals and pH change was studied at 30 °C, 35 g/L electrolyte and 7496 mg/L COD feed concentrations with 66.8 mA/cm^2 current density. The optimum residence time in the reactor was determined 6 h for a cost driven approach, enabling COD, color and turbidity removal as 44.3%, 86.2% and 87.1%, respectively, and a discharge pH value of 7.33. At 6 h of residence, 42 kWh energy was consumed per kg COD removed maintaining a mass transfer coefficient value of 3.62×10^{-6} m/s. In all runs, the polymer/water emulsion always broke into insoluble solid particles during the electrochemical treatment, which eventually precipitated.

1. Introduction

Paint is generally considered as a mixture of pigment, binder, solvent and additives, and the type and proportion of each component in the mixture characterize the properties of a particular paint. The components of paint also determine the characteristics of the waste generated in its manufacture and use [1–4].

A convenient method to classify paints is based on their primary solvent for waste reduction and disposal. In this respect, paints can be classified as water based, organic solvent based or powder (dry), without solvent [2]. The term “water based” refers to coating systems that use water as solvent to some extent. Water-based paints have advantages over some types of organic solvent based coatings because they generally decrease volatile organic carbon (VOC) emissions, eliminate organic solvents for thinning and reduce the use of organic solvents during clean-up. The major waste that paint industry must manage is dominantly equipment-cleaning wastes which make up 80% of the waste generated in paint manufacture [3].

In recent years, electrochemical oxidation is becoming a strong alternative for wastewater treatment because many industrial processes produce toxic wastewaters, which are not easily biodegradable and requiring costly physical or physico-chemical pretreatments [5]. Many researchers had investigated the electrochemical oxidation of various types of wastewater containing 1,4-benzoquinone [5], phenol [6–9], olive oil [10,11], vinasse [12], *p*-chlorophenol and *p*-nitrophenol [13], dichloromethane [14], 2-naphtol [15], ammonia [16], cadmium [17,18], nuclear wastes [19], human and domestic wastes [20,21], tannery wastewater [22,23] and textile wastewater [24–28], and metal recovery [29].

However, there is only one study dealing with electrochemical treatment of paint wastes in literature [30], other publications are only related to conventional treatment methods. In the study of Kutluay et al. [31] the chemical treatability of water-based industrial wastewater via adsorption was investigated and the authors concluded that highest chemical oxygen demand (COD) removal efficiency was achieved with sodium bentonite. Another study by Dovletoglou et al. [32] dealt with coagulation–flocculation of paint industry wastewater using ferrous and aluminum sulphate and polyaluminum chloride. El-Gohary et al. [33] also applied chemical treatment to paint factory wastewater for sedimentation using FeCl$_3$ in combination with CaO at optimum pH. The only work for bio-oxidation was carried out by Brown and Weintraub [34] in a laboratory scale continuous-flow-through reactor using cathodic electrocoating paint process wastewater, which was not toxic at all to the microorganisms in activated sludge process.

---

* Corresponding author. Tel.: +90 312 2977404; fax: +90 312 2992124.
E-mail addresses: korbahti@mersin.edu.tr (B.K. Körbahti), tanyolac@hacettepe.edu.tr (A. Tanyolaç).

1385-8947/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2008.09.019

Continuous electrochemical treatment studies were also scarce in literature. Sonoyama et al. [14] studied the continuous electrochemical decomposition of dichloromethane using a flow cell with Cu metal-powder column electrode. Alfafara et al. [16] treated brine wastewater with high ammonia content from an iodine processing plant by electrolysis in batch and continuous modes with indirect electrochemical treatment process via generating chlorine at the anodes. Grau and Bisang [17] examined the behavior of a continuous undivided electrochemical reactor with a rotating cylinder electrode. Sakalis et al. [27] investigated the electrochemical degradation of Reactive Orange 91, Reactive Red 184, Reactive Blue 182 and Reactive Black 5 azodyes using batch and continuous electrolytic cells with carbon fleece cathodes and Pt/Ti anodes, and sodium chloride and sodium sulfate electrolytes. In our previous study, the electrochemical treatment of phenolic wastewater was investigated in a continuous tubular reactor which was constructed of a stainless steel tube with a cylindrical carbon anode at the center [7].

In this work, the electrochemical treatment of water-based paint wastewater was investigated in a continuous tubular reactor with the presence of NaCl electrolyte on carbon anode and stainless steel cathode. In addition to possible electrochemical destruction of the paint components with undisclosed mechanisms, the presence of NaCl provided the discharge of chlorine gas and in return irreversible reactions of hydrolysis and ionization. With this study, application of the continuous tubular reactor for electrochemical oxidation of paint wastewater was realized for the first time in literature. The purpose of the present study was to investigate the effect of residence time on electrochemical treatment of paint industry wastewater. Additionally, the optimization of operating parameters for the electrochemical degradation of paint industry wastewater in a continuous tubular reactor was successfully accomplished using response surface methodology (RSM).

2. Materials and methods

2.1. Chemicals and materials

Acrylic copolymer water-based white primer was obtained from Marshall Boya Sanayi A.Ş., Kocaeli, Turkey. Water-based blue colorant was supplied from Polisan Boya Sanayi ve Ticaret A.Ş., Kocaeli, Turkey. Extra pure sodium chloride of Merck was utilized as additional electrolyte. Double distilled water was used for the preparation of synthetic water-based paint wastewater. All other chemicals used for the analysis were also obtained in highest degree of purity from various sources. Carbon electrodes (Meteor, Germany) used in the reactor (cylindrical, $D = 13.2$ mm) were originally designed and manufactured for DC electric motors to endure high voltage and current. Stainless steel 6R35 (Sandvik, Sweden) was used as cathode material (cylindrical, OD = 88.9 mm and wall thickness = 2 mm) with a weight % chemical composition 0.045 C, 0.40 Si, 1.18 Mn, 0.026 P, 0.001 S, 17.45 Cr, 10.14 Ni, 0.46 Ti, and the rest Fe.

2.2. Preparation and properties of synthetic water-based paint wastewater

The synthetic paint wastewater was prepared with 46.15 mL acrylic copolymer based white primer and 4.62 mL water-based blue colorant in a solution added up to 1 L using double distilled water, which corresponded to 4.4% (w/v) mixture. The characteristic of simulated water-based paint wastewater was presented in the previous study [30]. The original sample of discharged paint wastewater from a paint factory had COD, pH and total suspended solid values of 7863 mg/L, 7.84 and 3021 mg/L, respectively, with 4.4% (w/v) of total solid content.

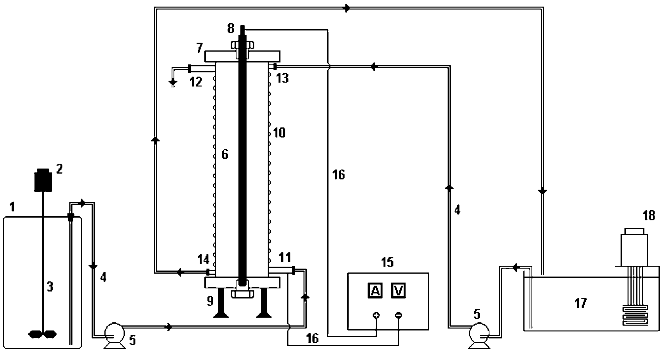

Fig. 1. The schematic view of the continuous electrochemical tubular reactor (1. wastewater reservoir, 2. driving motor, 3. glass stirrer, 4. feed lines, 5. peristaltic pumps, 6. electrochemical reactor, 7. Plexiglas reactor cover, 8. carbon electrode, 9. reactor support, 10. heating/cooling coil, 11. feed in, 12. feed out, 13. heating/cooling in, 14. heating/cooling out, 15. DC power source, 16. connections, 17. heating/cooling tank and 18. heater).

2.3. Experimental set-up and procedure

A continuous electrochemical tubular reactor was designed in our laboratory (Fig. 1) [35]. The 32 cm tall reactor (OD = 8.89 cm) had a net volume of 1774 cm^3 and was constructed of stainless steel (Sandvik, Sweden) with a heating/cooling coil around. The carbon electrode was used as the anode material and placed at the center of the reactor. The stainless steel wall of the reactor was used as cathode. A Cole Parmer model peristaltic Masterflex® pump was used to pump the paint wastewater from a 20 L reservoir. The reaction temperature was controlled with circulating water recycled from a temperature controlled water bath (New Brunswick, G-86) and monitored with glass thermometers immersed in the inlet and outlet of the column. The current was applied by a constant voltage/current controlled DC power source (NETES NPS-1810D).

Synthetic paint wastewater with the electrolyte was prepared in the wastewater reservoir at specified concentration and was fed to the column to fill it completely. An initial sample of 10 mL was taken from the reservoir to determine the initial COD concentration, color, turbidity and pH prior to the reaction. The reaction started with the application of the specified voltage and current, and the water for temperature control was recycled through the reactor coil while feed stream was pumped to the column continuously. At appropriate time intervals, samples of 5 mL were taken from the reactor outlet and analyzed to determine the intermediate properties of the reaction medium. DC power source was turned off and the reaction was terminated after 8 h of elapsed time.

2.4. Analysis

During the reaction 5 mL samples were taken from the electrochemical reactor at appropriate time intervals and pH was measured with a NEL pH30 model pH meter. Then the sample was centrifuged at 5000 rpm for 10 min to have supernatant for analysis and measurements. The color of the reaction medium was monitored by a Hitachi 150-20 model spectrophotometer at 595 nm and the turbidity was measured by a Hach 2100 AN IS model turbidimeter at 860 nm. COD analysis was performed with Palintest PL464 test kit after color and turbidity analysis. The samples were pretreated in order to prevent the interaction of Ag^+ ions in COD test kits with Cl^- ions remained in the sample as given previously [30].

2.5. Experimental optimization

In the study, the electrochemical degradation of paint industry wastewater in a continuous tubular reactor was optimized using response surface methodology (RSM) by Design-Expert® 7.1. The runs were designed in accordance with D-optimal design. The D-optimal criterion could be used to select points for a mixture design in a constrained region. This criterion selects design points from a list of candidate points so that the variances of the model regression coefficients are minimized [36,37].

The main purpose of the optimization part in the present study was to find a suitable approximating function in order to predict and determine the dependent variable response appropriately, and to investigate the operating conditions in a pre-determined region to optimize the selected goals under specified constraints.

The independent variables residence time and elapsed time were coded with low (1 h) and high levels (8 h) in D-optimal design, while COD, color and turbidity removals, pH, mass transfer coefficient and energy consumption were the responses (dependent variables). The D-optimal designed runs were augmented with three replications in order to evaluate the pure error and were carried in randomized order as required in many design procedures.

In the optimization process, the response can be simply related to chosen factors by linear or quadratic models. A quadratic model, which also includes the linear model, is given as

$$\eta = \beta_0 + \sum_{j=1}^{k}\beta_j x_j + \sum_{j=1}^{k}\beta_{jj} x_j^2 + \sum_{i}\sum_{<j=2}^{k}\beta_{ij} x_i x_j + e_i \qquad (1)$$

where η is the response, k is the number of factors, x_i and x_j are variables, β_0 is the constant coefficient, βj's, β_{jj}'s and β_{ij}'s are interaction coefficients of linear, quadratic and the second-order terms, respectively, and e_i is the error [36,37]. In the study, the data was processed for Eq. (1) including ANOVA to obtain the interaction between the process variables and the response. The quality of the fit of polynomial model was expressed by the coefficient of determination R^2 and R^2_{adj}. The statistical significance was checked with adequate precision ratio, F-values and P-values.

In the optimization, a module in Design-Expert® 7.1 software searched for a combination of factor levels that simultaneously satisfy the requirements placed on each of the responses and factors. The desired goals were selected as maximum COD, color and turbidity removal percents at minimum residence time and minimum energy consumption. Corresponding importances of goals were selected as 5 for COD removal, color removal and energy consumption, 3 for residence time, elapsed time, pH and mass transfer coefficient, and 2 for turbidity removal. These individual goals were combined into an overall desirability function by Design-Expert® 7.1 software for maximization to find the best local maximum.

3. Results and discussions

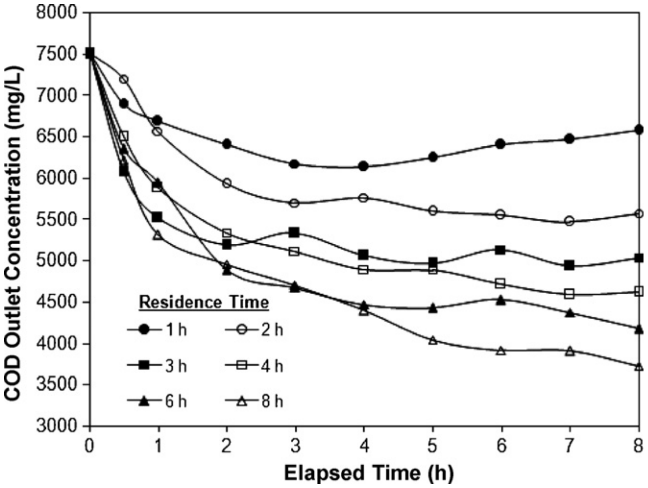

Fig. 2. The COD concentration profiles in the tubular reactor (current density: 66.8 mA/cm^2; T: 30 °C; electrolyte concentration: 35 g/L).

Experiments were carried out to determine the effects of the residence time on COD, color and turbidity removals, and pH change of the paint wastewater, as well as on mass transfer coefficient and power consumption. All runs were carried out under optimized reaction conditions determined previously through batch runs [30]. These optimized conditions were 35 g/L NaCl concentration, 30 °C reaction temperature and 64.37 mA/cm^2 current density at 7496 mg/L initial COD concentration. In all continuous runs, the COD feed concentration was 7496 mg/L with 35 g/L electrolyte concentration and 66.8 mA/cm^2 current density at 30 °C reaction temperature. In every run, the polymer/water emulsion was always broken into insoluble solid particles. In the study only the soluble COD in the supernatant was measured, therefore the solid particles were not analyzed.

3.1. The effect of residence time on electrochemical degradation

The discharge COD concentration, color and turbidity, and pH were determined at the column reactor outlet for 1, 2, 3, 4, 6 and 8 h of residence time as appeared in figures. In Fig. 2, the COD removal was realized as 12.3%, 25.7%, 32.9%, 38.5%, 44.3% and 50.3% for 1, 2, 3, 4, 6 and 8 h residence time, respectively, at the end of 8 h elapsed time. In Fig. 2 all COD profiles except that of 1 h residence almost reached at steady state. The color and turbidity removals determined at the reactor outlet are shown in Figs. 3 and 4, respectively. For 1 h of residence time after 4 h, maximum color and turbidity removals were obtained as 74.7% and 72.3%, respectively, and then these values fluctuated between 40.1–63.8% for color removal and 30.4–61.4% for turbidity removal. Similar trends were also observed for 2 h residence time and color and turbidity removals fluctuated between 55.6–70.8% and 57.5–71.9%, respectively, after 3 h. During electrochemical treatment it was concluded that organic molecules were electrooxidized at the anode or electroreduced at the cathode forming smaller intermediate molecules. In electrochemical

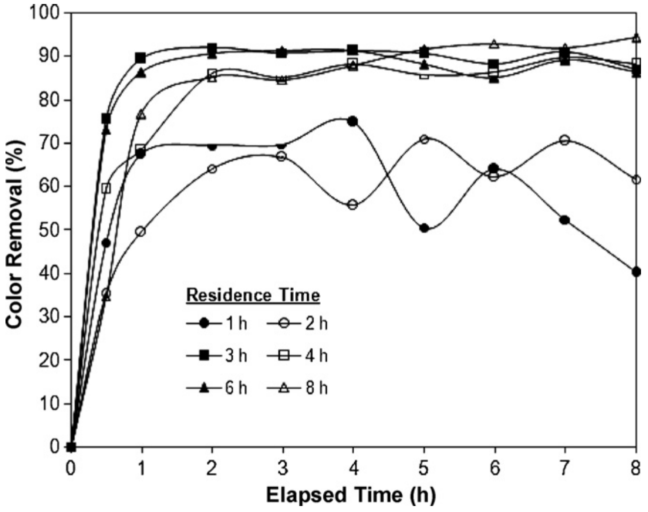

Fig. 3. The color removal profiles in the tubular reactor (current density: 66.8 mA/cm^2; T: 30 °C; electrolyte concentration: 35 g/L).

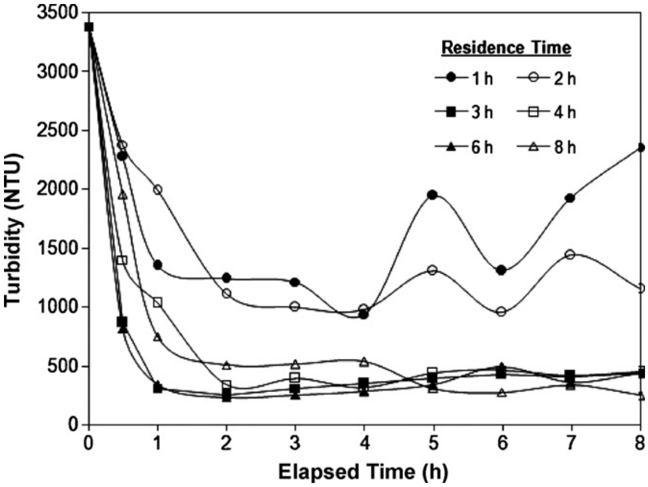

Fig. 4. The turbidity profiles in the tubular reactor (current density: 66.8 mA/cm^2; *T*: 30 °C; electrolyte concentration: 35 g/L).

treatment, COD, color and turbidity removals in the presence of NaCl electrolyte were also realized by indirect electrolysis generating in situ active chlorine (Cl_2, $HOCl/ClO^-$). Any residence time shorter than 2 h leads to increase in the concentration of low molecular weight organic compounds, which may possibly contribute to the turbidity. Nevertheless, for residence time above 2 h, both color and turbidity removals showed smooth increasing profiles with non-fluctuating nature. In Figs. 3 and 4, the color and turbidity removals were realized as 40.1%, 30.4%; 61.6%, 66.0%; 87.0%, 87.0%; and 88.0%, 86.9%; 86.2%, 87.1%, 94.3%, 92.8% for 1, 2, 3, 4, 6 and 8 h residence time, respectively, at the end of 8 h. Apparently, increasing residence time resulted in steady profiles of removal with higher treatment performances.

The approximating functions of dependent variables (factors) COD ($\hat{y}_1$), color ($\hat{y}_2$) and turbidity ($\hat{y}_3$) removal percents obtained with D-optimal design in this study are presented in Eqs. (2)–(4).

$$\hat{y}_1 = 5.676x_1 + 8.218x_2 + 0.504x_1x_2 - 0.503x_1^2 - 0.892x_2^2 - 5.396 \qquad (2)$$

$$\hat{y}_2 = 12.141x_1 + 21.336x_2 + 0.668x_1x_2 - 1.269x_1^2 - 2.416x_2^2 + 9.321 \qquad (3)$$

$$\begin{aligned}\hat{y}_3 = {} & 16.394x_1 + 22.422x_2 + 0.587x_1x_2 \\ & -1.631x_1^2 - 2.540x_2^2 - 0.779 \end{aligned} \qquad (4)$$

In Eqs. (2)–(4), x_1 was residence time (h) in the reactor and x_2 was elapsed time (h) during the electrolysis. ANOVA results of these quadratic models are presented in Table 1. In the table, model *F*-values of 104.80, 20.64 and 23.04 imply the models are significant for COD, color and turbidity removal percents, respectively. For all equations, adequate precision signal to noise ratio is greater than 4, which is desirable for sound models. Also for all models, *P*-values are less than 0.0001, indicating that terms are significant in all models while correlation coefficients denote good enough quadratic fits to navigate the design space. The normal % probability and studentized residuals graphs for responses $\hat{y}_1$, $\hat{y}_2$ and $\hat{y}_3$ yielded fair straight lines, proving normal distribution of the data (the graphs were not shown).

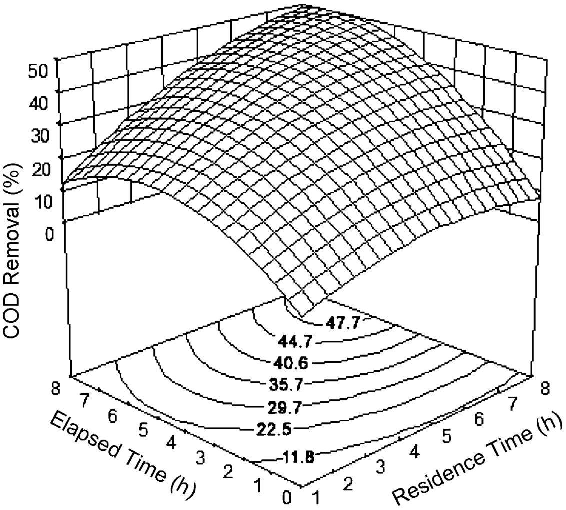

Fig. 5. The effect of residence time on COD removal (current density: 66.8 mA/cm^2; *T*: 30 °C; electrolyte concentration: 35 g/L).

Eqs. (2)–(4) have been used to visualize the effects of experimental factors on responses under optimized conditions in response surface graphs of Figs. 5–7. In Fig. 5, COD removal percent increased by increasing residence time and maximum COD removal obtained at 8 h residence time in the reactor for elevated elapsed time. However, 6 h of residence time is good enogh for complete color and turbidity removals as observed in Figs. 6 and 7.

Fig. 8 shows the pH profile at the outlet of the tubular reactor where pH was not controlled. As a general trend, pH sharply decreased in 30 min down to pH 7.0–7.8 from 8.7, and then continued to drop to neutral pH gradually. This trend was observed in all runs and was most likely due to hydrolysis, ionization and OCl^- consumption reactions, in which H^+ is a by-product. Nevertheless, instable pH values were observed due to incomplete reactions in the reactor within the time range of runs as well as non-homogeneous character of the reactor. In Fig. 8, the pH values at the discharge were obtained as 7.16, 6.97, 6.93, 7.25, 7.33 and 7.05 at 1, 2, 3, 4, 6 and 8 h of residence time, respectively, after 8 h.

Although there has not been any work done yet with electrochemical treatment of paint wastewater in literature using the

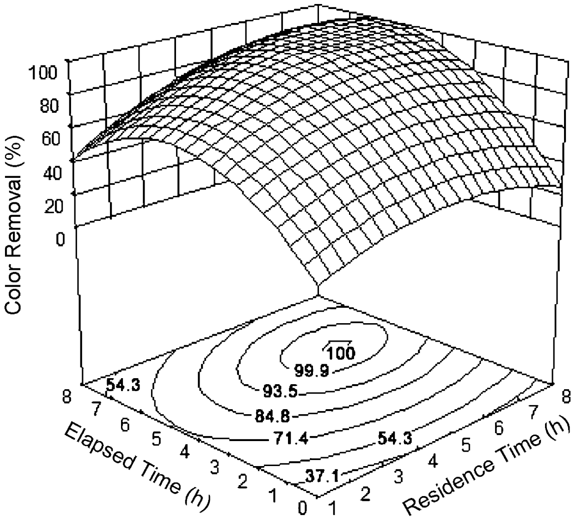

Fig. 6. The effect of residence time on color removal (current density: 66.8 mA/cm^2; *T*: 30 °C; electrolyte concentration: 35 g/L).

Table 1
ANOVA results of the quadratic models for COD, color and turbidity removal percents, mass transfer coefficient and energy consumption.

Source	Sum of squares	Degrees of freedom	Mean square	*F*-value	*P*-value
COD removal (%)[a]					
Model	10231.91	5	2046.38	104.80	<0.0001
x_1: residence time (h)	3545.09	1	3545.09	181.55	<0.0001
x_2: elapsed time (h)	4047.79	1	4047.79	207.30	<0.0001
x_1x_2	613.50	1	613.50	31.42	<0.0001
x_1^2	352.13	1	352.13	18.03	<0.0001
x_2^2	1581.84	1	1581.84	81.01	<0.0001
Residual	1054.44	54	19.53		
Color removal (%)[b]					
Model	30022.23	5	6004.45	20.64	<0.0001
x_1: residence time (h)	5710.13	1	5710.13	19.63	<0.0001
x_2: elapsed time (h)	9203.16	1	9203.16	31.63	<0.0001
x_1x_2	1076.39	1	1076.39	3.70	0.0597
x_1^2	2243.03	1	2243.03	7.71	0.0075
x_2^2	11618.22	1	11618.22	39.93	<0.0001
Residual	15710.95	54	290.94		
Turbidity removal (%)[c]					
Model	33161.81	5	6632.36	23.04	<0.0001
x_1: residence time (h)	8527.68	1	8527.68	29.62	<0.0001
x_2: elapsed time (h)	8320.93	1	8320.93	28.90	<0.0001
x_1x_2	831.41	1	831.41	2.89	0.0950
x_1^2	3704.85	1	3704.85	12.87	0.0007
x_2^2	12841.21	1	12841.21	44.61	<0.0001
Residual	15545.44	54	287.88		
Mass transfer coefficient (m/s)[d]					
Model	1.850×10^{-10}	5	3.700×10^{-11}	64.99	<0.0001
x_1: residence time (h)	5.752×10^{-11}	1	5.752×10^{-11}	101.03	<0.0001
x_2: elapsed time (h)	7.224×10^{-11}	1	7.224×10^{-11}	126.88	<0.0001
x_1x_2	1.532×10^{-12}	1	1.532×10^{-12}	2.69	0.1067
x_1^2	2.902×10^{-12}	1	2.902×10^{-12}	5.10	0.0280
x_2^2	3.766×10^{-11}	1	3.766×10^{-11}	66.14	<0.0001
Residual	3.074×10^{-11}	54	5.694×10^{-13}		
Energy consumption (kWh/kg COD removed)[e]					
Model	2.747×10^{5}	5	54935.63	40.41	<0.0001
x_1: residence time (h)	96043.47	1	96043.47	70.65	<0.0001
x_2: elapsed time (h)	1.514×10^{5}	1	1.514×10^{5}	111.38	<0.0001
x_1x_2	30063.28	1	30063.28	22.12	<0.0001
x_1^2	45352.45	1	45352.45	33.36	<0.0001
x_2^2	642.74	1	642.74	0.47	0.4946
Residual	73404.30	54	1359.34		

[a] $R^2 = 0.91$; $R^2_{adj} = 0.90$; adequate precision = 35.87.

[b] $R^2 = 0.66$; $R^2_{adj} = 0.62$; adequate precision = 15.31.

[c] $R^2 = 0.68$; $R^2_{adj} = 0.65$; adequate precision = 16.98.

[d] $R^2 = 0.86$; $R^2_{adj} = 0.84$; adequate precision = 28.65.

[e] $R^2 = 0.79$; $R^2_{adj} = 0.77$; adequate precision = 25.97.

tubular reactor to compare with our results, there are other works carried out in different systems for paint wastewater treatment. In literature, Kutluay et al. [31] investigated treatability of water-based industrial paint wastewater by adsorption using sodium bentonite. Their work resulted in 84–94% COD removal with 500 mg/L sodium bentonite concentration at original pH of the wastewater with an initial COD value of 1200 mg/L. They also achieved 92–100% color removal using sodium bentonite with 300–1000 mg/L dosages at pH 9, 10 and at original wastewater pH [31]. Dovletoglou et al. [32] determined the optimum pH 9.7 for $FeSO_4$ addition at a dose of 2 g/L, and achieved 30–80% COD removal for an initial COD of 128 ± 88 g/L via coagulation/flocculation. In their runs, no pH adjustment was needed when $Al_2(SO_4)_3$ was used at a dose of 2.5 g/L, which yielded 70–95% COD removal. They also achieved turbidity removal as 70–99%, 90–99% and 98% with the addition of $FeSO_4$, $Al_2(SO_4)_3$ and polyaluminum chloride, respectively. Moreover, their separation process required 4 min for the addition of coagulant, 25 min for flocculation and 30 min for settling, which in total was faster than our removal rate [32]. El-Gohary et al. [33] also applied physicochemical treatment to the paint factory wastewater using 50 mg/L $FeCl_3$ in combination with 140 mg/L CaO at the optimum pH 8.2 and they obtained 90% COD removal of an average initial COD value of 1590 mg/L. Brown and Weintraub [34] obtained COD reduction as 39% and 87% for residence times of 1.2 and 2.4 days for an initial COD of 900–1000 mg/L, respectively, with activated sludge treatment of paint process wastewater. Huang and Ghadirian [38] applied coagulation/flocculation to wastewater samples from a paint manufacturing plant, and they obtained 70% COD removal at pH 3.5, while only 35% removal was achieved at alkaline pH. In terms of COD removal, some of literature studies apparently achieved better results than our work, however, this success was granted at the expense of rather high concentration of coagulants and adsorbents requiring pH adjustment and, more importantly, their processes were merely physical separation.

3.2. *Mass transfer coefficient*

As the wastewater flows through the tubular reactor, the concentrations of the electroactive species decrease due to reactions occur on the electrodes and in the solution. This depletion depends

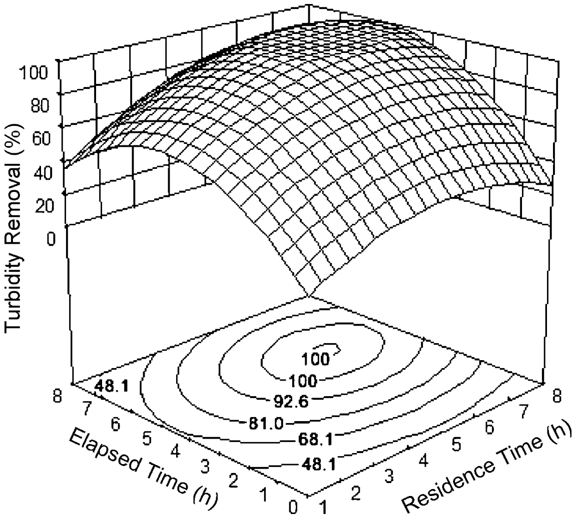

Fig. 7. The effect of residence time on turbidity removal (current density: 66.8 mA/cm^2; T: 30 °C; electrolyte concentration: 35 g/L).

on the electrode potential, length of the electrode, flow rate, and the ratio of electrode area and electrolyte volume. In a flow reactor, a reaction layer next to the electrode surface forms with a concentration gradient where its thickness is a function of "current/mass transport controlled limiting current ratio" and the Reynolds number [39,40].

In an electrochemical reactor, mass transfer coefficient is related to the physical parameters of the system including the solution properties. In general, the cell and electrode arrangements are so complex that specification of the velocity and concentration variations with time and location cannot be made accurately [41]. Therefore, general correlations in engineering literature to express the mass transfer coefficient as Sherwood number in terms of Schmidt and Reynolds numbers may lead to unrealistic mass transfer coefficients for laminar flow [39,40]. Nevertheless, in a reactor it is possible to characterize the mass transport regime as a function of flow rate and cell and electrode dimensions. Mass transfer coefficient for a single pass plug flow reactor could be estimated by Eq. (5), which is a mass balance over the reactor via Faraday's law. The equation holds valid with the assumption that the entire electrode supports a reaction under mass transport control via convective diffusion of the reactant or product and the longitudinal dispersion of flow due to diffusion is negligible [39,41];

$$x_{\mathrm{PFR}} = 1 - \exp\left[\left(\frac{-k_{\mathrm{m}}A}{V_{\mathrm{R}}}\right)\tau_{\mathrm{R}}\right] \qquad (5)$$

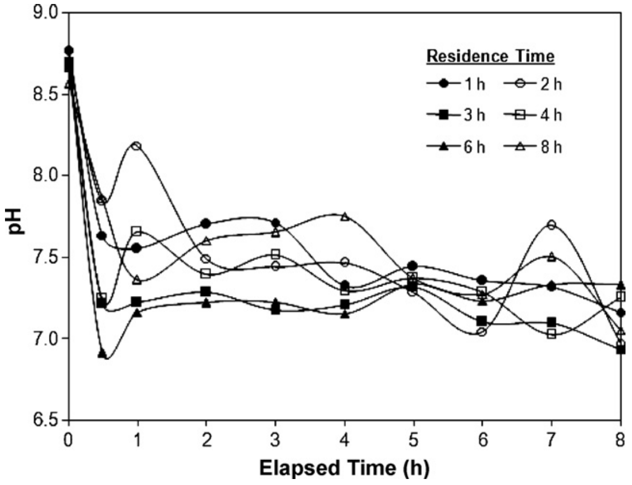

Fig. 8. The pH profiles in the tubular reactor (current density: 66.8 mA/cm^2; T: 30 °C; electrolyte concentration: 35 g/L).

In Eq. (5), V_{R} is internal reactor volume, A is the electrode area, k_{m} is mass transfer coefficient, τ_{R} is average residence time, and x_{PFR} is fractional COD conversion. In Eq. (6), the approximating function of mass transfer coefficient ($\hat{y}_4$) obtained with D-optimal design is given. In Table 1, the model F-value, P-value and adequate precision value imply that the quadratic model is significant for the mass transfer coefficient.

$$\begin{aligned}\hat{y}_4 = {} & -7.319\times10^{-7}x_1 + 1.616\times10^{-6}x_2 - 2.519\times10^{-8}x_1x_2 \\ & +4.566\times10^{-8}x_1^2 - 1.376\times10^{-7}x_2^2 + 2.696\times10^{-6}\end{aligned} \qquad (6)$$

The changes of Reynolds number, k_{m} and fractional COD conversion with residence time in the tubular reactor are presented in Table 2. As the residence time increased, fractional COD conversion increased because of extended reaction time. The flow in the tubular reactor was in the range of 1.11×10^{-5} to 8.89×10^{-5} m/s indicating that flow regime in the column was laminar for corresponding Re numbers between $0.9 < Re < 6.9$. Eq. (5) was derived at both time-independent inlet and outlet COD concentrations in the case of a steady state reactor. Consequently, the results estimated with Eq. (5) should be in the case of steady state. However, as can be seen in Fig. 2, for 1 h residence time COD outlet concentration continued to rise indicating an unestablished flow regime/steady state. Therefore, the mass transfer coefficient estimated for 1 h residence time could be ignored. For residence time values greater than 1 h, k_{m} decreased with increasing residence time i.e. decreasing linear velocity and Reynolds number. The film resistance i.e. stagnant film thickness around the electrodes proportionally increases with decreasing flow rate within the reactor resulting in diminished mass transfer rate [39]. Other factors affecting the k_{m} can be the length of the entry section where hydrodynamic boundary layer is still developing and gas evolution at the electrodes. The gas discharge may introduce a complex iR drop in the electrolyte, which is also sensitive to the prevailing hydrodynamics [39]. k_{m} values decreased with decreased flow rate however increasing retention time enabled higher overall mass transport to the electrodes.

Although there has not been any literature work done yet to compare the results of this study, there are estimated mass transfer coefficients in different investigations. Morão et al. [9] studied the electrochemical oxidation of multi-component mixtures of organic compounds using boron doped diamond anode and obtained mass transfer coefficients for phenol, phenyl-methanol, 1-phenyl-ethanol and m-cresol degradation as 1.9×10^{-5}, 1.9×10^{-5}, 1.7×10^{-5} and 2.1×10^{-5} m/s, respectively. Panizza and Cerisola [15] investigated the electrochemical oxidation of 2-naphthol using lead dioxide, boron-doped diamond and Ti–Ru–Sn ternary oxide anodes, and determined the mass transfer coefficient in the range 0.7×10^{-5} to 2.0×10^{-5} m/s. Fernandes et al. [28] studied the electrochemical oxidation of C. I. Acid Orange 7 on a boron doped diamond electrode and calculated an average mass transfer coefficient of 1.46×10^{-5} m/s. Mass transfer coefficient values experienced in this study had the same order of magnitude with those of literature data related to electrochemical treatment.

3.3. Energy consumption

The energy consumption during the electrochemical treatment is given in the last column of Table 2, where E is the overall mean

Table 2
The change of system characteristics as a function of residence time in the continuous tubular reactor.

Residence time (h)	Linear velocity ($\times 10^5$ m/s)	Fractional COD conversion	*Re*	k_m ($\times 10^6$ m/s)	*E* (kWh/kg CODr)
1	8.89	0.123	6.90	4.88	167.30
2	4.44	0.257	3.45	5.51	82.64
3	2.96	0.329	2.30	4.93	51.90
4	2.22	0.385	1.72	4.51	42.01
6	1.48	0.443	1.15	3.62	41.96
8	1.11	0.503	0.86	3.25	79.39

energy consumption up to stabilized conversion. The *E* was relatively high at 1 h of residence time as 167.3 kWh/kg COD removed due to unsettled steady state conditions and low conversion. In Table 2, the energy consumption decreased with the increase in residence time up to 6 h, and above 6 h of residence time increased with enhanced residence time. The minimum energy consumption was obtained for 6 h of residence time as 42 kWh/kg COD removed while the residence time at 6 h was also determined as the optimum according to Figs. 6 and 7. Thus electrochemical tubular reactor must be operated at 6 h of residence time for a cost driven approach with 35 g/L electrolyte addition and 66.8 mA/cm^2 current density at 30 °C reaction temperature. These conditions ensured COD, color and turbidity removals as 44.3%, 86.2% and 87.1%, and a discharge pH value of 7.33, respectively, with a prevailing mass transfer coefficient of 3.62×10^{-6} m/s.

The approximating function of energy comsumption ($\hat{y}_5$) obtained with D-optimal design is given in Eq. (7). In Table 1, the model *F*-value, *P*-value and adequate precision value imply that the quadratic model is significant for energy comsumption.

$$\hat{y}_5 = -50.645x_1 + 28.540x_2 - 3.528x_1x_2 + 5.708x_1^2 + 0.568x_2^2 + 90.626 \qquad (7)$$

In the literature, the mean energy consumption was determined as 1.273–12.3, 12.4, 4.8–200, 21 and 1.273–12.3 kWh/kg COD removed for the electrochemical treatment of olive oil wastewater [11], domestic wastewater [21], tannery waste liquors [23], textile dye wastewater [25,26] and noncyanide strippers wastes [42] in a re-circulated tubular batch reactor consisted of 304 stainless steel cathode and Ti/Pt anode placed at the center of the reactor, respectively.

3.4. Optimization of experimental conditions

The results were optimized by Design-Expert® 7.1 using the approximating functions in Eqs. (2)–(4) and Eqs. (6)–(7). In the optimization, residence time and energy consumption were minimized for a cost driven approach within 0–8 h of elapsed time, whereas COD, color and turbidity removal percents were maximized at 100% pollution load (COD = 7496 mg/L). The optimization resulted in 6 h residence time and 5 h elapsed time with the prediction of pH 7.1, 44.0% COD, complete color and turbidity removals. Under these optimized conditions, mass transfer coefficient and energy consumption were estimated as 3.87×10^{-6} m/s and 42.1 kWh/kg COD removed, respectively. The results of the RSM optimization were in a reasonable prediction with the results obtained experimentally.

4. Conclusion

The electrochemical treatment of industrial water-based paint wastewater in a continuous tubular reactor constructed from a stainless steel tube with a cylindrical carbon anode at the center was investigated. The effects of residence time on COD, color and turbidity removals and pH change of the reaction medium were studied at 30 °C, 35 g/L electrolyte concentration and 7496 mg/L COD feed concentration with 66.8 mA/cm^2 current density. Steady state conditions started to prevail with increased residence time which also led to enhanced COD, color and turbidity removal efficiencies. The COD, color and turbidity removals were realized 12.3%, 40.1%, 30.4%; 25.7%, 61.6%, 66.0%; 32.9%, 87.0%, 87.0%; 38.5%, 88.0%, 86.9% and 44.3%, 86.2%, 87.1%, 50.3%, 94.3%, 92.8% for 1, 2, 3, 4, 6 and 8 h of residence time, respectively, after 8 h. As a general trend the outlet pH sharply decreased within 30 min down to pH 7.0–7.8 from 8.7, and then continued to drop to neutral pH gradually in proportion with the residence time in the tubular reactor. This trend was observed in all runs and was most likely due to hydrolysis, ionization and OCl^- consumption reactions. Optimum residence time for minimum energy consumption was determined as 6 h, estimating COD, color and turbidity removals as 44.3%, 86.2% and 87.1%, respectively, and a discharge pH value of 7.33 with the expense of 42 kWh/kg COD removed. The results indicate that the continuous tubular reactor could be a feasible and an effective alternative system for the electrochemical treatment of industrial paint wastewater, whereas it could also be used at an oxidation pretreatment stage for the detoxification of the wastewater and breaking the polymer/water emulsions.

Acknowledgement

This project was supported by DPT (State Planning Organization of the Turkish Republic Prime Ministry) with Grant No. 02.K.120.290-15.

References

[1] Center for Economics Research, Paint waste reduction and disposal options, vol. I, Research Triangle Institute, HWRIC RR-060, Urbana, 1992.
[2] Center for Economics Research, Paint waste reduction and disposal options, Executive summary, Research Triangle Institute, HWRIC TR-007, Urbana, 1992.
[3] The Massachusetts Toxics Use Reduction Institute, Substitution Case Study: Alternatives to solvent-based paints, Technical Report No. 4, University of Massachusetts, Lowell, 1993.
[4] Center for Economics Research, Paint waste reduction and disposal options, vol. II: Site visits, Research Triangle Institute, HWRIC TR-008, Urbana, 1993.
[5] C. Pulgarin, N. Adler, P. Péringer, Ch. Comninellis, Electrochemical detoxification of a 1,4-benzoquinone solution in wastewater treatment, Water Res. 28 (1994) 887–893.
[6] J. Iniesta, P.A. Michaud, M. Panizza, G. Cerisola, A. Aldaz, Ch. Comninellis, Electrochemical oxidation of phenol at boron-doped diamond electrode, Electrochim. Acta 46 (2001) 3573–3578.
[7] B.K. Körbahti, A. Tanyolaç, Continuous electrochemical treatment of phenolic wastewater, Water Res. 37 (2003) 1505–1514.
[8] Ch. Comninellis, A. Nerini, Anodic oxidation of phenol in the presence of NaCl for wastewater treatment, J. Appl. Electrochem. 25 (1995) 23–28.
[9] A. Morão, A. Lopes, M.T. Pessoa de Amorim, I.C. Gonçalves, Degradation of mixtures of phenols using boron doped diamond electrodes for wastewater treatment, Electrochim. Acta 49 (2004) 1587–1595.
[10] M. Gotsi, N. Kalogerakis, E. Psillakis, P. Samaras, D. Mantzavinos, Electrochemical oxidation of olive oil mill wastewaters, Water Res. 39 (2005) 4177–4187.
[11] C.J. Israilides, A.G. Vlyssides, V.N. Mourafetti, G. Karvouni, Olive oil wastewater treatment with the use of an electrolysis system, Bioresour. Technol. 61 (1997) 163–170.

[12] A.G. Vlyssides, C.J. Israilides, M. Loizidou, G. Karvouni, V. Mourafetti, Electrochemical treatment of vinasse from beet molasses, Water Sci. Technol. 36 (1997) 271–278.

[13] C. Borras, T. Laredo, B.R. Scharifker, Competitive electrochemical oxidation of *p*-chlorophenol and *p*-nitrophenol on Bi-doped PbO_2, Electrochim. Acta 48 (2003) 2775–2780.

[14] N. Sonoyama, K. Ezaki, T. Sakata, Continuous electrochemical decomposition of dichloromethane in aqueous solution using various column electrodes, Adv. Environ. Res. 6 (2001) 1–8.

[15] M. Panizza, G. Cerisola, Influence of anode material on the electrochemical oxidation of 2-naphthol. Part 2. Bulk electrolysis experiments, Electrochim. Acta 49 (2004) 3221–3226.

[16] C.G. Alfafara, T. Kawamori, N. Nomura, M. Kiuchi, M. Matsumura, Electrolytic removal of ammonia from brine wastewater: scale-up, operation and pilot-scale evaluation, J. Chem. Technol. Biotechnol. 79 (2004) 291–298.

[17] J.M. Grau, J.M. Bisang, Removal of cadmium and production of cadmium powder using a continuous undivided electrochemical reactor with a rotating cylinder electrode, J. Chem. Technol. Biotechnol. 77 (2002) 465–472.

[18] J.M. Grau, J.M. Bisang, Removal of cadmium from dilute aqueous solutions with a rotating cylinder electrode of expanded metal, J. Chem. Technol. Biotechnol. 78 (2003) 1032–1037.

[19] J.O'M. Bockris, J. Kim, Electrochemical treatment of low level nuclear wastes, J. Appl. Electrochem. 27 (1997) 623–634.

[20] C.L.K. Tennakoon, R.C. Bhardwaj, J.O'M. Bockris, Electrochemical treatment of human wastes in a packed bed reactor, J. Appl. Electrochem. 26 (1996) 18–29.

[21] A.G. Vlyssides, P.K. Karlis, N. Rori, A.A. Zorpas, Electrochemical treatment in relation to pH of domestic wastewater using Ti/Pt electrodes, J. Hazard. Mater. B95 (2002) 215–226.

[22] L. Szpyrkowicz, S.N. Kaul, R.N. Neti, S. Satyanarayan, Influence of anode material on electrochemical oxidation for the treatment of tannery wastewater, Water Res. 39 (2005) 1601–1613.

[23] A.G. Vlyssides, C.J. Israilides, Detoxification of tannery waste liquors with an electrolysis system, Environ. Pollut. 97 (1997) 147–152.

[24] L. Szpyrkowicz, C. Juzzolino, S.N. Kaul, A comparative study on oxidation of disperse dyes by electrochemical process, ozone, hypochlorite and Fenton Reagent, Water Res. 35 (2001) 2129–2136.

[25] A.G. Vlyssides, M. Loizidou, P.K. Karlis, A.A. Zorpas, D. Papaioannou, Electrochemical oxidation of a textile dye wastewater using a Pt/Ti electrode, J. Hazard. Mater. B70 (1999) 41–52.

[26] A.G. Vlyssides, D. Papaioannou, M. Loizidoy, P.K. Karlis, A.A. Zorpas, Testing an electrochemical method for treatment of textile dye wastewater, Waste Manage. 20 (2000) 569–574.

[27] A. Sakalis, K. Mpoulmpasakos, U. Nickel, K. Fytianos, A. Voulgaropoulos, Evaluation of a novel electrochemical pilot plant process for azodyes removal from textile wastewater, Chem. Eng. J. 111 (2005) 63–70.

[28] A. Fernandes, A. Morão, M. Magrinho, A. Lopes, I. Gonçalves, Electrochemical degradation of C. I. Acid Orange 7, Dyes Pigments 61 (2004) 287–296.

[29] M. Spitzer, R. Bertazzoli, Selective electrochemical recovery of gold and silver from cyanide aqueous effluents using titanium and vitreous carbon cathodes, Hydrometallurgy 74 (2004) 233–242.

[30] B.K. Körbahti, N. Aktaş, A. Tanyolaç, Optimization of electrochemical treatment of industrial paint wastewater with response surface methodology, J. Hazard. Mater. 148 (2007) 83–90.

[31] G. Kutluay, F.G. Babuna, G. Eremektar, D. Orhon, Treatability of water-based paint industry effluents, Fresen. Environ. Bull. 13 (2004) 1057–1060.

[32] O. Dovletoglou, C. Philippopoulos, H. Grigoropoulou, Coagulation for treatment of paint industry wastewater, J. Environ. Sci. Health A37 (2002) 1361–1377.

[33] F.A. El-Gohary, R.A. Wahaab, F.A. Nasr, H.I. Ali, Three Egyptian industrial wastewater management programmes, Environmentalist 22 (2002) 59–65.

[34] J.A. Brown, M. Weintraub, Biooxidation of paint process wastewater, J. Water Pollut. Control Fed. 54 (1982) 1127–1130.

[35] B.K. Körbahti, System design and process development for electrochemical treatment of industrial water-based paint wastewater and textile wastewater, PhD Dissertation, Hacettepe University, Ankara-Turkey, 2003.

[36] D.C. Montgomery, Design and Analysis of Experiments, fourth ed., John Wiley & Sons, USA, 1996.

[37] R.H. Myers, D.C. Montgomery, Response Surface Methodology: Process and Product Optimization Using Designed Experiments, second ed., John Wiley & Sons, USA, 2002.

[38] C.P. Huang, M. Ghadirian, Physical–chemical treatment of paint industry wastewater, J. Water Pollut. Control Fed. 46 (1974) 2340–2346.

[39] D. Pletcher, F.C. Walsh, Industrial Electrochemistry, second ed., Chapman and Hall, New York, 1990.

[40] M.I. Ismail, Electrochemical Reactors: Their Science and Technology, Part A, Elsevier, Amsterdam, 1989.

[41] K. Rajeshwar, J.G. Ibanez, Environmental Electrochemistry, Academic Press, San Diego, 1996.

[42] A.G. Vlyssides, P.K. Karlis, A.A. Zorpas, Electrochemical oxidation of noncyanide strippers wastes, Environ. Int. 25 (1999) 663–670.