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Optimization of electrochemical treatment of industrial paint wastewater with response surface methodology

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Abstract

The electrochemical oxidation of water-based paint wastewater was investigated batch-wise in the presence of NaCl electrolyte with carbon electrodes for the first time in literature. The electrochemical treatment conditions were optimized using response surface methodology where potential difference, reaction temperature and electrolyte concentration were to be minimized while chemical oxygen demand (COD), color and turbidity removal percents and initial COD removal rate were maximized at 100% pollution load. The optimum conditions were satisfied at 35 g/L external electrolyte concentration, 30 °C reaction temperature and 8 V potential difference (64.37 mA/cm² current density) realizing 51.8% COD and complete color and turbidity removals, and 3010.74 mg/L h initial COD removal rate. According to these results, the electrochemical method could be a strong alterative to conventional physicochemical methods for the treatment of water-based paint wastewater.
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1. Introduction

Paint is generally considered as a mixture of pigment, binder, solvent and additives. Paint classification can be made on many different bases; one convenient method is to classify paints based on their primary solvent for waste reduction and disposal. Using this approach, paints can be classified as water based, organic solvent based or powder (dry) and without solvent [1]. Water-based paints have advantages over some types of organic solvent based coatings because they generally decrease 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 makes up 80% of the waste generated in paint manufacture [2].

In recent years, electrochemical oxidation is becoming an alternative for wastewater treatment and starting to replace traditional processes, because many industrial processes produce toxic wastewaters, which are not easily biodegradable and requiring costly physical or physico-chemical pretreatments [3]. Many researchers had investigated the electrochemical oxidation of various types of wastewater containing 1,4-benzoquinone [3], phenol [4–6], olive oil [7], vinasse [8], *p*-chlorophenol and *p*-nitrophenol [9], nuclear wastes [10], human wastes [11], tannery wastewater [12] and textile wastewater [13,14].
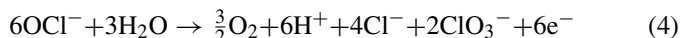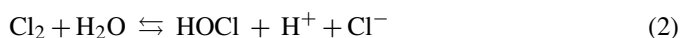
However, there is a lack of research dealing with electrochemical treatment of paint wastes in literature; present publications are only related to conventional treatment methods. A recent study by Kutluay et al. investigated the chemical treatability of water-based industry wastewater via adsorption and the authors concluded that highest COD removal efficiency was achieved with sodium bentonite [15]. Another study by Dovletoglou et al. dealt with coagulation–flocculation of paint industry wastewater using ferrous and aluminum sulphate and polyaluminum chloride [16]. El-Gohary et al. also applied chemical treatment

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to paint factory wastewater for sedimentation using $FeCl_3$ in combination with CaO at optimum pH [17]. The only work for biooxidation was carried out by Brown and Weintraub 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 [18].

In electrochemical treatment, COD, color and turbidity removal in the presence of NaCl electrolyte were carried out mainly by indirect electrolysis generating in situ active chlorine (Cl_2, $HOCl/ClO^-$). The discharged chlorine gas (reaction (1)) [8,19–21] was in excess amount in the reactor and the irreversible reactions of hydrolysis (reaction (2)) [19,21,22] and ionization take place (reaction (3)) [19,22]. Hypochlorous acid, HOCl, is a strong oxidant, which oxidizes the wastewater while OCl^- is also consumed by reaction (4) [8,23,24]:

$$2Cl^- \rightarrow Cl_2 + 2e^- \tag{1}$$

$$Cl_2 + H_2O \leftrightarrows HOCl + H^+ + Cl^- \tag{2}$$

$$HOCl \leftrightarrows H^+ + OCl^- \tag{3}$$

$$6OCl^- + 3H_2O \rightarrow \tfrac{3}{2}O_2 + 6H^+ + 4Cl^- + 2ClO_3^- + 6e^- \tag{4}$$

In this study, electrochemical treatment of a simulated water-based paint wastewater was optimized in the presence of NaCl on carbon electrodes using response surface methodology by Design-Expert 6 (trial version). The runs were designed in accordance with the central composite design and carried out batch-wise. The water-based paint wastewater was synthetically prepared from industrial components for the standardization of the wastewater throughout the study. Five factors: pollution load percent, potential difference, electrolyte concentration, reaction temperature and reaction time were selected as effective process (independent) variables while COD, color and turbidity removal percents and initial COD removal rate as responses (dependent variable).

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.

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

The 100% polluted synthetic wastewater was prepared having 46.15 mL acrylic copolymer based white primer and 4.62 mL water-based blue colorant in a solution added up to 1 L with double distilled water, which corresponded to 4.4% (w/v) mixture. The characteristics of simulated water-based paint wastewater is

Table 1
The characteristics of simulated industrial water-based paint wastewater

Parameter	Value
Chemical oxygen demand (mg/L)	7496
Turbidity (NTU)	3378
pH	9.12
Dissolved oxygen (mg/L)	6.16
Total solids (mg/L)	43,370
Total suspended solids (mg/L)	2770
Total dissolved solids (mg/L)	40,600
Total volatile solids (mg/L)	4460
Non-volatile solids (mg/L)	38,910
Total solid content (%)	4.24
Conductivity (μS)	394 (=444.1 μS/cm)
Density (g/cm^3)	1.024

presented in Table 1 whereas the original sample of discharged paint wastewater from a paint factory had values of COD, pH and total suspended solids as 7863, 7.84 and 3021 mg/L, respectively, with 4.4% (w/v) of total solid content. The characteristics of paint wastewater in literature studies were reported as, COD 459–19,000 mg/L, pH 6.7–7.5, turbidity 500 NTU, conductivity 1400 μS/cm, total solids 168–240 mg/L [15–18,25]. In the runs for concentration effect, the wastewater was accordingly diluted in regard with the composition (100%) in Table 1 with double distilled water.

2.3. Experimental set-up and procedure

The electrochemical reactor system was used batch-wise in all runs. The reactor was made of Pyrex® glass having a net volume of 600 mL with a heating/cooling coil around. Three pairs of carbon electrodes (OD = 12 mm) were used as anode and cathode, and placed 1.5 cm apart on a Plexiglas® reactor cover. A glass stirrer with a single 4 cm × 1.5 cm rectangular paddle was driven with a Heidolph-RZR 1 model mixer at 575 rpm. The reaction temperature was monitored with a glass thermometer immersed and controlled with circulating water recycled from a temperature controlled water bath (New Brunswick, Model G-86). The current was applied by a constant voltage/current controlled dc power source (NETES Model NPS-1810D). Synthetic paint wastewater was loaded into the reactor and the reaction under predetermined conditions started with the application of specified voltage and continuous agitation. At appropriate time intervals, samples of 5 mL were taken from the reactor and analyzed to determine the chemical oxygen demand, color, turbidity and pH.

2.4. Experimental design and optimization

The most popular class of second order designs called central composite design (CCD) was used for the response surface methodology in the experimental design. The CCD is ideal for sequential experimentation and allows a reasonable amount of information for testing lack of fit while not involving an unusually large number of design points [26]. Therefore, the CCD with five factors at five levels was applied using Design-Expert

Table 2
Experimental results of CCD designed experiments

Run no.	x_1 (%)	x_2 (V)	x_3 (g/L)	x_4 (°C)	x_5 (h)	COD removal (%)	Color removal (%)	Turbidity removal (%)	COD initial removal rate (mg COD/h L)
1	80	8	12.5	40	6	29.00	98.92	96.99	681.84
2	80	8	12.5	30	6	25.21	98.49	97.08	1112.92
3	40	8	37.5	40	6	50.36	97.91	97.69	1934.82
4	80	4	12.5	30	6	5.52	25.51	18.13	271.68
5	60	6	25.0	35	8	42.28	97.98	94.69	546.92
6	40	8	12.5	40	2	26.58	96.86	95.94	651.68
7	40	8	37.5	40	2	43.80	98.57	89.86	1934.82
8	40	4	37.5	30	2	23.17	89.40	86.91	408.56
9	40	4	37.5	30	6	40.29	97.72	98.08	408.56
10	60	6	25.0	35	4	35.09	99.11	97.67	1576.12
11	80	8	37.5	30	2	38.17	97.80	96.17	2761.76
12	60	6	25.0	35	4	35.39	99.15	96.73	546.92
13	40	4	12.5	40	2	5.23	40.54	18.88	250.44
14	60	6	0.0	35	4	6.77	25.53	35.40	172.20
15	60	2	25.0	35	4	1.24	31.60	10.57	125.56
16	60	6	50.0	35	4	49.39	98.88	96.05	678.32
17	40	4	12.5	30	2	10.38	45.03	33.31	374.60
18	60	6	25.0	35	4	36.01	99.11	97.63	836.64
19	60	6	25.0	35	4	32.86	99.37	97.92	948.44
20	60	6	25.0	35	4	25.97	98.01	96.85	167.28
21	40	4	37.5	40	6	23.75	94.91	95.39	414.24
22	40	4	37.5	40	2	10.46	78.44	67.86	414.24
23	100	6	25.0	35	4	29.09	99.75	99.08	667.92
24	60	10	25.0	35	4	46.35	98.90	96.78	2600.80
25	80	4	37.5	40	6	18.54	93.81	84.84	368.96
26	80	8	37.5	30	6	54.77	99.00	99.77	2761.76
27	60	6	25.0	35	4	35.09	99.11	97.67	1576.12
28	80	4	12.5	30	2	4.13	18.11	16.88	271.68
29	20	6	25.0	35	4	49.32	98.13	94.86	791.84
30	40	8	12.5	40	6	26.98	96.86	97.45	651.68
31	40	8	37.5	30	2	48.95	96.57	96.10	1477.84
32	40	8	37.5	30	6	65.68	98.74	96.56	1477.84
33	60	6	25.0	45	4	27.11	98.98	96.63	661.08
34	80	4	12.5	40	2	3.02	37.47	12.57	244.48
35	80	4	37.5	40	2	5.65	56.41	34.67	368.96
36	60	6	25.0	35	4	36.01	99.11	97.63	836.64
37	60	6	25.0	25	4	36.09	98.12	94.33	938.64
38	60	6	25.0	35	0	0	0	0	0
39	40	4	12.5	40	6	13.07	70.19	61.33	250.44
40	80	8	37.5	40	2	42.24	98.94	95.78	3160.96
41	40	8	12.5	30	6	42.49	98.43	97.36	1028.12
42	60	6	25.0	35	4	32.86	99.37	97.92	948.44
43	80	8	12.5	30	2	15.17	80.50	79.74	1112.92
44	80	8	37.5	40	6	52.79	99.46	98.05	3160.96
45	80	4	37.5	30	6	24.35	96.50	94.36	675.20
46	80	4	12.5	40	6	11.49	80.51	57.71	244.48
47	40	8	12.5	30	2	31.64	91.55	89.53	1028.12
48	80	4	37.5	30	2	8.05	46.73	24.86	675.20
49	40	4	12.5	30	6	14.00	65.52	51.53	374.60
50	80	8	12.5	40	2	17.87	84.53	75.63	681.84

6.0. Each independent variable was coded at five levels between −2 and +2, where the variables pollution load (x_1), potential difference (x_2), electrolyte concentration (x_3), reaction temperature (x_4) and reaction time (x_5) were changed in the ranges 20–100%, 2–10 V, 0–50 g/L, 25–45 °C and 0–8 h, respectively. The critical ranges of selected parameters were determined by preliminary experiments based on literature experience.

Forty-two experiments were augmented with eight replications at the design center to evaluate the pure error and were carried in randomized order as required in many design procedures. First six columns of Table 2 show run number and experimental conditions of the runs arranged by the CCD. Performance of the process was evaluated by analyzing the responses; COD, color and turbidity removal percents and COD initial removal rate.

In the optimization process, the responses are related to factors by quadratic models, which also include the linear model as shown in Eq. (5), where η is the response, x_i and x_j are vari-

ables, β_0 the constant coefficient, β_js, 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:

$$\eta = \beta_0 + \sum_{j=1}^{k}\beta_j x_j + \sum_{j=1}^{k}\beta_{jj}x_j^2 + \sum_{i}\sum_{<j=2}^{k}\beta_{ij}x_i x_j + e_i \quad (5)$$

COD, color, turbidity removal percent and initial COD removal rate data were processed for Eq. (5) using Design-Expert 6.0 program including ANOVA to obtain the interaction between the process variables and the response. The coefficients of determination R^2 and R_{adj}^2 expressed the quality of fit of the resultant polynomial model, and statistical significance was checked by F-test in the program. For optimization, a module in Design-Expert 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, turbidity and color removal percents, and maximum initial COD removal rate at minimum reaction temperature, electrolyte concentration and potential difference within the range of reaction time at 100% pollution load. Corresponding importances of goals were selected as 5 for COD, color and turbidity removal percents and initial COD removal rate; 3 for pollution load, potential difference, electrolyte concentration and reaction time, and 1 for reaction temperature. These individual goals were combined into an overall desirability function by Design-Expert software for maximization to find the best local maximum [27].

2.5. 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 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 performed with Palintest PL464 test kit after color and turbidity analysis. In order to prevent the precipitation of Ag^+ ions in COD test kits with Cl^- ions present in the sample, the samples were pre-treated with appropriate volumes of 2 M $AgNO_3$ prior to COD analysis. AgCl precipitated and the sample was centrifuged at 5000 rpm for 10 min. The supernatant was removed and the precipitate was washed with 0.5 mL pure sulphuric acid for desorption of the adsorbed waste and centrifuged at 5000 rpm for 10 min. This procedure was repeated twice. All of the collected supernatants were volumetrically measured, mixed and 1 mL of the sample mixture was added to COD kit for digestion. Grant QBT2 model block heater was set to 150 °C and sample and blank tubes were digested for 2 h. Then the tubes were allowed to cool down to room temperature and the absorbance of the samples was read at 605 nm. The COD of the samples was calculated using a calibration curve prepared previously taking the dilutions into account in washing steps.
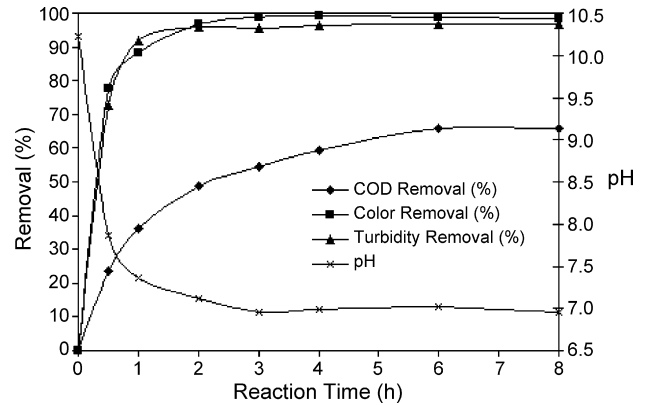

Fig. 1. COD, color and turbidity removal profiles for run 32 (pollution load: 40%; potential difference: 8 V; electrolyte concentration: 37.5 g/L; reaction temperature: 30 °C).

3. Results and discussion

Fifty CCD designed batch runs were conducted to visualize the effects of independent factors on responses and the results along with the experimental conditions were presented in Table 2. More than 35% COD removal was realized in 20 runs while over 90% color and turbidity removals were achieved in more than 30 runs of Table 2. As a general trend, increase in electrolyte concentration and potential difference resulted in enhanced COD, color and turbidity removals and COD initial removal rate in all runs.

In Table 2, run 32 specifically gave the best removal for COD as 65.68% while more than 95% removal of color and turbidity was achieved in the same run after 8 h, although initial COD removal rate was not realized as high as in runs 40 and 44 performed at 40 °C. Fig. 1 shows COD, color and turbidity removal percent and pH time profiles in this run. In Fig. 1, above 90% of color and turbidity removal achieved within 2 h of reaction time indicating more efficient removal of color and turbidity than that of COD. In Fig. 1, medium pH decreased from 10.2 to 7.0 within 3 h, being an advantage for neutralization of treated water without using any chemical. 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 [21].

3.1. Evaluation of experimental results with Design-Expert

Experimental results were evaluated with Design-Expert 6.0 using approximating functions of dependent variables COD (y_1), color (y_2), turbidity (y_3) removal percents and initial COD removal rate (y_4). These approximating functions are presented in Eqs. (6)–(9):

$$y_1 = -23.770 - 1.436x_1 + 10.705x_2 + 0.994x_3 + 0.974x_4$$
$$+9.960x_5 + 0.0027x_1^2 - 0.692x_2^2 - 0.0109x_3^2$$
$$-0.0327x_4^2 - 0.858x_5^2 - 0.0013x_1x_2 - 0.0004x_1x_3$$
$$+0.0255x_1x_4 + 0.0086x_1x_5 + 0.118x_2x_3 + 0.0194x_2x_4$$
$$+0.0152x_2x_5 - 0.0203x_3x_4 + 0.0704x_3x_5 - 0.0672x_4x_5$$

$$(6)$$

$$y_2 = -22.689 - 2.756x_1 + 39.895x_2 + 6.360x_3 - 5.727x_4$$
$$+27.718x_5 + 0.0057x_1^2 - 1.533x_2^2 - 0.0441x_3^2$$
$$+0.0878x_4^2 - 2.549x_5^2 + 0.0850x_1x_2 + 0.0022x_1x_3$$
$$+0.0300x_1x_4 + 0.0690x_1x_5 - 0.288x_2x_3 - 0.177x_2x_4$$
$$-1.328x_2x_5 - 0.0434x_3x_4 - 0.0308x_3x_5 + 0.0831x_4x_5$$
$$(7)$$

$$y_3 = -86.406 - 2.232x_1 + 47.709x_2 + 6.106x_3 - 3.994x_4$$
$$+25.306x_5 + 0.0038x_1^2 - 2.328x_2^2 - 0.0403x_3^2$$
$$+0.0456x_4^2 - 2.723x_5^2 + 0.116x_1x_2 - 0.0012x_1x_3$$
$$+0.0169x_1x_4 + 0.0731x_1x_5 - 0.345x_2x_3 - 0.0441x_2x_4$$
$$-1.588x_2x_5 - 0.0308x_3x_4 + 0.0218x_3x_5 + 0.215x_4x_5$$
$$(8)$$

$$y_4 = 6445.725 - 30.048x_1 - 865.595x_2 - 121.539x_3$$
$$-129.600x_4 + 174.846x_5 + 0.0263x_1^2 + 42.210x_2^2$$
$$-0.420x_3^2 + 1.120x_4^2 - 20.669x_5^2 + 3.926x_1x_2$$
$$+0.681x_1x_3 - 0.205x_1x_4 + 12.838x_2x_3 + 3.129x_2x_4$$
$$+1.514x_3x_4 \qquad (9)$$

In Eqs. (6)–(9) x_1, x_2, x_3, x_4, and x_5 are corresponding to independent variables of pollution load, potential difference, electrolyte concentration, reaction temperature and reaction time, respectively. ANOVA results of these quadratic models are presented in Table 3. In the table, model F-values of 34.93, 9.92, 15.50 and 10.25 imply the models are significant for COD, color, turbidity removal percents and initial COD removal rate, respectively. For all equations, adequate precision signal-to-noise ratio is greater than 4, which is desirable for sound models. Also for all models, Prob > F is less than 0.0001, indicating that terms are significant in all models while correlation coefficient changed in the range 0.94–0.98 denoting good enough quadratic fits to navigate the design space. Normal % probability and studentized residuals graphs for responses y_1–y_4 yielded fair straight lines, proving normal distribution of the data.

3.2. Optimization of experimental conditions

The results were optimized by Design-Expert software using the approximating functions in Eqs. (6)–(9). In optimization, a cost driven approach was preferred in the range of 25–45 °C reaction temperature within 0–8 h of reaction time; potential difference, reaction temperature and electrolyte concentration were to be minimized so as to save energy and electrolyte, whereas COD, color and turbidity removal percents and initial COD removal rate were maximized at 100% pollution load. The optimization results are shown in Table 4 in accord with descending desirability whereas PD, EC, T, t, CR, ICR and D are corresponding to potential difference, electrolyte concentration, reaction temperature, reaction time, COD removal percent, initial COD removal rate and desirability, respectively.

Optimized conditions under specified constraints were obtained for highest desirability at 100% pollution load, 35 g/L electrolyte concentration, 30 °C reaction temperature and 8 V potential difference (64.37 mA/cm² current density) after 6.79 h of reaction time. Under these optimized conditions, 51.8% COD removal, 100% color and turbidity removals and 3010.74 mg/L h initial COD removal rate were estimated. In order to validate the optimization, a specific batch run was performed under these optimum conditions. In this run, COD, color and turbidity removals, and initial COD removal rate were realized as 68.7%, 99.3%, 99.1% and 2748.9 mg/L h, respectively, proving predictive power of the model approach, although COD removal was underestimated.

3.3. Effects of operational parameters at optimum conditions

Eqs. (6)–(9) have been used to visualize the effects of experimental factors on responses under optimized conditions in 3D graphs of Figs. 2–6. In Fig. 2, COD removal percent increased by increasing electrolyte concentration and potential difference above 11.8 g/L and 4 V (5.16 mA/cm² current density), respectively, and more than 60% COD removal was realized at 100% pollution load and 30 °C reaction temperature within 8 h of reaction time above 7.5 V potential difference (43.88 mA/cm² current density) and 38.9 g/L electrolyte concentration. Increasing electrolyte concentration and voltage increased the conductivity and current simultaneously, which in turn enhanced the reaction rate of electrochemical destruction. Moreover, since the presence of NaCl in the reaction medium generates in situ very strong oxidants of HOCl/ClO⁻ increase of electrolyte concentration and voltage directly increase the concentration of these chemicals in the medium enabling faster COD, color and turbidity removal [8,19,21–24].

In Fig. 3, COD removal decreased below 80% pollution load by increasing reaction temperature but was not affected above this percent. At low temperatures COD removal increased by
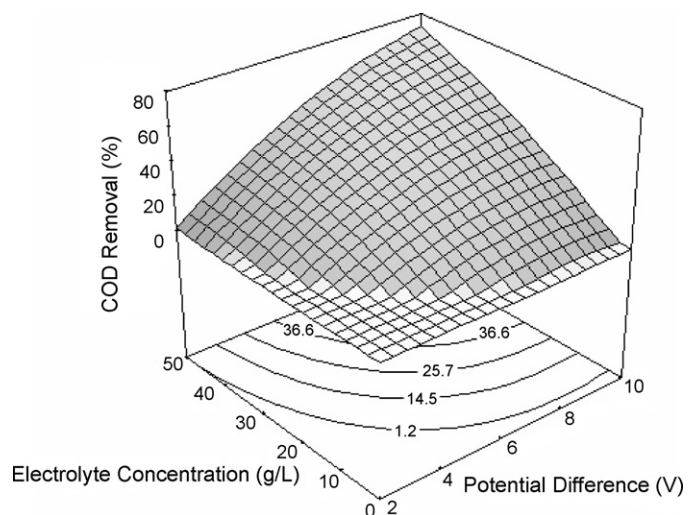

Fig. 2. The effect of potential difference and electrolyte concentration on COD removal (pollution load: 100%; reaction temperature: 30 °C; reaction time: 8 h).

Table 3
ANOVA results of the quadratic models for COD, color and turbidity removal percents and initial COD removal rate

Source	Sum of squares	Degrees of freedom	Mean square	F-Value	Prob $> F$
COD removal (%)					
Model	12742.63	20	637.13	34.93	<0.0001
Residual	528.97	29	18.24		
Lack of fit	450.42	22	20.47	1.82	0.2111
Pure error	78.54	7	11.22		
$R^2 = 0.96$, $R^2_{adj} = 0.93$, adequate precision = 25.59					
Color removal (%)					
Model	31175.46	20	1558.77	9.92	<0.0001
Residual	4554.75	29	157.06		
Lack of fit	4553.44	22	206.97	1105.68	<0.0001
Pure error	1.31	7	0.19		
$R^2 = 0.87$, $R^2_{adj} = 0.78$, adequate precision = 13.01					
Turbidity removal (%)					
Model	42795.99	20	2139.80	15.50	<0.0001
Residual	4004.71	29	138.09		
Lack of fit	4003.25	22	181.97	872.59	<0.0001
Pure error	1.46	7	0.21		
$R^2 = 0.91$, $R^2_{adj} = 0.86$, adequate precision = 14.79					
Initial COD removal rate (mg/L h)					
Model	2.749×10^7	20	1.374×10^6	10.25	<0.0001
Residual	3.888×10^6	29	1.341×10^5		
Lack of fit	2.307×10^6	22	1.048×10^5	0.46	0.9201
Pure error	1.582×10^6	7	2.259×10^5		
$R^2 = 0.88$, $R^2_{adj} = 0.79$, adequate precision = 12.17					

pollution load implying a positive order of magnitude of waste concentration in overall kinetics. As a general rule, the reaction rate increases as the temperature increases, however the increase in temperature did not have a significant effect on COD removal, in fact caused a visible drop for lower COD load percents. In Fig. 3, higher COD removal was realized at lower reaction temperatures. At higher temperatures with low pollution load, this behavior could be attributed to the inhibition of electrochemical oxidation and/or increasing corrosion rate of the electrodes as well as to more conversion of electrical energy into heat due to increased resistance of the medium at high temperatures. Above 90% pollution load at 30 °C, 8 V potential difference and 35 g/L electrolyte concentration, a region of more than 50% COD removal was achieved within 8 h of reaction time. In literature there is limited number of studies for comparison, but they were accomplished via biodegradation and mostly coagula-

tion/sedimentation, not by electrochemical destruction. Brown and Weintraub obtained COD reduction as 39% and 87% for residence times of 1.2 and 2.4 days, respectively, with activated sludge treatment of paint process wastewater [18]. Huang and Ghadirian 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 [25]. Dovletoglou et al. determined the optimum pH 9.7 for FeSO$_4$ addition at a dose of 2 g/L, and achieved 30–80% COD removal via coagulation/flocculation while no pH adjustment was needed using Al$_2$(SO$_4$)$_3$ at a dose of 2.5 g/L, which yielded 70–95% COD removal [16]. El-Gohary et al. also applied physicochemical treatment to the paint factory wastewater using 50 mg/L FeCl$_3$ in combination with 140 mg/L CaO at an optimum pH 8.2 and they obtained 90% COD removal [17]. Kutluay et al. investigated treatability of water-based industrial

Table 4
Optimization results for maximum treatment

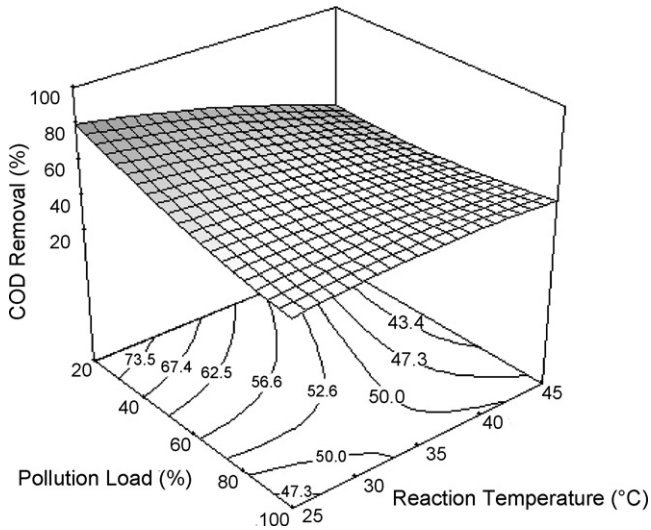| Solution no.	PD (V)	EC (g/L)	T (°C)	t (h)	CR (%)	Color removal (%)	Turbidity removal (%)	ICR (mg/L h)	D
1	7.96	36.44	29.8	6.79	51.8	100	100	3007.88	0.64
2	7.96	36.43	29.8	6.81	51.7	100	100	3006.16	0.64
3	7.96	36.41	29.8	6.78	51.7	100	100	3002.94	0.64
4	7.96	36.44	29.8	6.78	51.8	100	100	3005.61	0.64
5	7.96	36.45	29.9	6.80	51.8	100	100	3010.74	0.64
6	7.96	36.40	29.9	6.80	51.8	100	100	3005.31	0.64
7	7.95	36.46	29.9	6.79	51.8	100	100	3004.11	0.64

Fig. 3. The effect of reaction temperature and pollution load on COD removal (potential difference: 8 V; electrolyte concentration: 35 g/L; reaction time: 8 h).

Fig. 5. The effect of potential difference and electrolyte concentration on turbidity removal (pollution load: 100%; reaction temperature: 30 °C; reaction time: 3 h).

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 [15]. In terms of COD removal, some of literature studies apparently achieved better results than this work, however, this success was granted at the expense of rather high concentration of coagulants and adsorbents requiring pH adjustment and their processes were merely separation rather than destruction.

In Fig. 4, above 7 V potential difference (32.33 mA/cm^2 current density) complete color removal was obtained between 9.4 and 44.9 g/L electrolyte concentration at 100% pollution load and 30 °C reaction temperature within 3 h. Kutluay et al. achieved 92–100% color removal using sodium bentonite with 300–1000 mg/L dosages at pH 9, 10 and original wastewater pH. In Fig. 5, complete turbidity removal was obtained above 7.4 V potential difference (41.28 mA/cm^2 current density) for 5.5–40.2 g/L electrolyte concentration at 100% pollution load

Fig. 6. The effect of reaction temperature and pollution load on turbidity removal (potential difference: 8 V; electrolyte concentration: 35 g/L; reaction time: 3 h).

and 30 °C reaction temperature within 3 h of reaction time. In Fig. 6 within 3 h reaction time, complete turbidity removal was realized below 33 °C at 100% pollution load, 8 V potential difference, 35 g/L electrolyte concentration. In literature, Dovletoglou et al. 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, with the addition of coagulant for 4 min, flocculation for 25 min and settling for 30 min of time, which is shorter than our removal rate [16].

4. Conclusion

The electrochemical treatment of synthetic industrial water-based paint wastewater was studied in a batch reactor with carbon electrodes in the presence of NaCl electrolyte. The highest removals for COD, color and turbidity were realized 65.68%
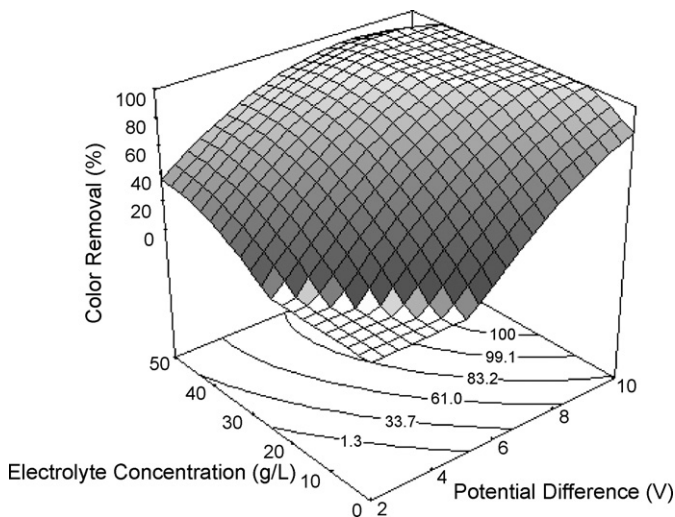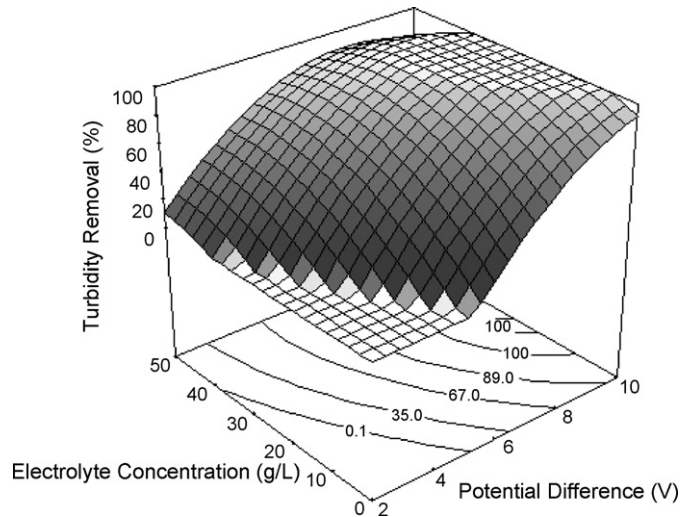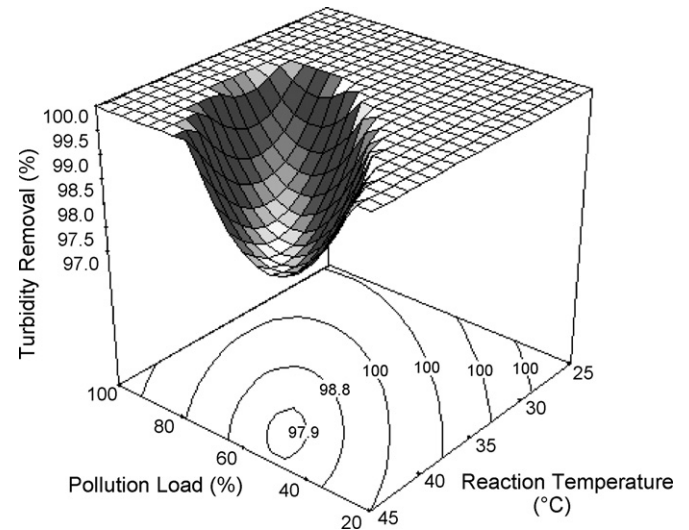

Fig. 4. The effect of potential difference and electrolyte concentration on color removal (pollution load: 100%; reaction temperature: 30 °C; reaction time: 3 h).

98.74% and 96.56%, respectively. The approximating functions for COD, color, turbidity and initial COD removal rate were obtained with high degrees of fit. Electrochemical treatment conditions were optimized using RSM and in this respect, potential difference, reaction temperature and electrolyte concentration were minimized while COD, color and turbidity removal percents and initial COD removal rate were maximized at 100% pollution load. The optimum conditions were satisfied at 100% pollution load, 35 g/L external electrolyte concentration, 30 °C reaction temperature and 8 V potential difference (64.37 mA/cm^2 current density) realizing 51.8% COD removal and complete color and turbidity removals, and 3010.74 mg/L h initial COD removal rate. According to these results, the electrochemical method could be a valuable alterative to conventional physicochemical methods for the treatment of water-based paint wastewater with further research.

Acknowledgement

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