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Electrochemical degradation of three reactive dyes using carbon paper cathode modified with carbon nanotubes and their simultaneous determination by partial least square method

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Abstract−We investigated the treatment of a mixture of three reactive textile dyes (C. I. Reactive Red 195, C. I. Reactive Yellow 84 and C. I. Reactive Blue 69) by electro-Fenton (EF) process using carbon paper cathode modified with carbon nanotubes (CNTs). To study the degradation of mixture of three dyes, a rapid analytical methodology based on recording UV-Vis spectra during the EF process and the data treatment using partial least square (PLS) as a multivariate calibration method was developed. The three reactive dyes were quantified simultaneously despite the overlap of their spectra. Central composite design was used in the modeling and optimization of the electrochemical decolorization process. The independent variables for modeling were initial concentration of three dyes, applied current in the electrolysis system, and reaction time. Results indicated that the optimum applied current value was about 400 mA for the EF process. Analysis of variance (ANOVA) showed that predicted responses by CCD match the experimental values logically with the amount of R^2 more than 0.92.

Keywords: Electrochemical Treatment, Carbon Nanotubes, Spectrophotometric Determination, Carbon Paper, Central Composite Design

INTRODUCTION

Over the last decade, among the different technologies applied for the degradation of toxic and/ or bio-refractory organics in water, electrochemical advanced oxidation processes (EAOPs), such as electro-Fenton (EF) and photoelectro-Fenton (PEF), have received increasing attention [1-4]. The main advantages of EAOPs are their environmental compatibility, versatility, high efficiency, amenability of automation and safety due to their use at mild conditions. The EF and PEF technologies involve the continuous supply of hydrogen peroxide to an acidic contaminated medium from the two-electron reduction of injected O_2 at the cathode surface (Eq. (1)) [5]:

$$O_2+2H^++2e^-\rightarrow H_2O_2 \qquad (1)$$

The use of carbonaceous materials has been highly regarded for environmental remediation [6,7]. In the field of EAOPs, good efficiencies for H_2O_2 electro-generation from reaction (1) have been reported using carbonaceous cathodes such as carbon nanotubes-polytetrafluoroethylene (PTFE) [8,9], carbon nanotubes on graphite [5] and carbon paper [10], carbon sponge [11], carbon felt [12] and carbon-PTFE gas (O_2 or air) diffusion [13,14].

In the EF process, the oxidation ability of electro-generated H_2O_2 is strongly increased by adding a catalytic amount of Fe^{2+} (or Fe^{3+}) ion to react with H_2O_2 and yield homogeneous $^{\bullet}OH$ and Fe^{3+} ion from Fenton's reaction (Eqs. (2) and (3)) [15]:

$$Fe^{2+}+H_2O_2+H^+\rightarrow Fe^{3+}+{}^{\bullet}OH+H_2O \qquad (2)$$

$$Fe^{3+}+e^-\rightarrow Fe^{2+} \qquad (3)$$

The produced $^{\bullet}OH$ as a strong oxidant with high standard reduction potential can non-selectively oxidize most organics and give dehydrogenated or hydroxylated derivatives, which can be mineralized totally. An advantage of EF compared to the classical chemical Fenton process is that reaction (2) is propagated by the cathodic reduction of Fe^{3+} to Fe^{2+} by reaction (3) [16].

In recent years, EF and related electrochemical technologies have been developed to remove various pollutants from wastewater with the aim of preserving the aquatic environment. Dyestuffs are one of the important categories of organic compounds, and their degradation behavior has been investigated by these methods. Most of the produced synthetic organic dyes are used in the textile industry, leather tanning industry, paper production, food technology, agricultural research, and light-harvesting arrays, as well as in hair colorings. The majority of dyestuffs consumed by various industries are azo derivatives, although anthraquinone, indigoid, arylmethane, and xanthene compounds are frequently utilized. The discharge of high contents of colored effluents into water bodies like lakes and rivers cause not only aesthetic problems linked to wastewater color, but also health risks to human beings and environmental damage by impeding light penetration, and due to toxicity, carcinogenicity, potential mutagenicity and resistance to biodegradation of these pollutants and their by-products [15,17]. So, research efforts are needed for the introduction and development of powerful treatment pro-

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cesses to destroy organic dyes and their by-products from wastewaters in order to avoid their adverse impacts.

Despite many studies having been performed to remove just one dye from aqueous solutions, little research has been done on the removal of a mixture of dyes [2,18-20]. But, since a colorful effluent usually contains a mixture of several dyes, the treatment of a mixture of dyes is necessary. So, in the present study, the removal of mixture of three reactive dyes widely used in textile industry (C. I. Reactive Red 195, C. I. Reactive Yellow 84 and C. I. Reactive Blue 69) was investigated by EF process using a carbon paper cathode modified with CNTs. Due to the overlap of dye spectra in the mixture, the usual univariate calibration method could not be used for determination of dye concentration. So a statistical and chemometric method, namely partial least square (PLS), was used for analysis of the set of spectra obtained in the UV-Vis region and simultaneous determination of the dyes in related mixtures. Also, response surface methodology (RSM) was used to study the influence of operational parameters on the decolorization efficiency of three dyes by the EF process.

MATERIALS AND METHODS

1. Chemicals

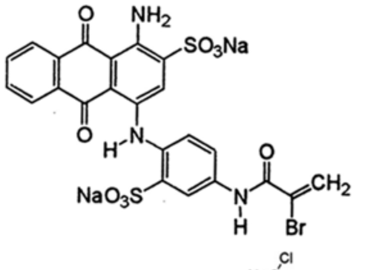
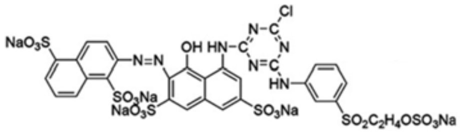
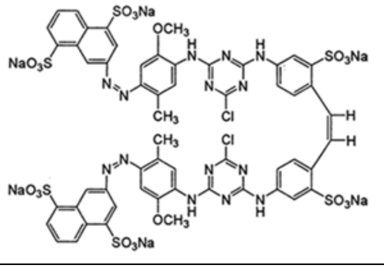
The synthetic and commercial dyes (C. I. Reactive Red 195 (RR195), C. I. Reactive Yellow 84 (RY84) and C. I. Reactive Blue 69 (RB69)) were purchased from Ciba-Geigy (Switzerland) and were used without further purification. The structure and characteristics of the dyes are presented in Table 1. Carbon paper (TGP-H-060, thick: 190 μm, conductivity: 12.5 S/cm, bulk density: 0.44 g/cm^3 and porosity: 80%) and multi walled carbon nanotubes (outer diameter: 10-20 nm, inside diameter: 3-5 nm, length: 10-30 μm, bulk density: 0.22 g/cm^3, conductivity: >100 S/cm and purity: >95 wt%) were purchased from Toray (Japan) and Cheap Tubes Inc. (USA), respectively. All other chemicals used in this study were of the analytical grade and obtained from Merck (Germany). Sodium sulfate (Na_2SO_4) was used as support electrolyte.

2. Instruments and General Procedure

The fabrication of carbon paper cathode modified with CNTs has been explained in our previous works [10,21]. In summary, an appropriate amount of CNTs (0.1 g), 0.42 g PTFE, 60 mL distilled water and 3% n-butanol was mixed in an ultrasonic bath (Grant, England) for 20 min to obtain a highly dispersed mixture. The resulting mixture after heating at 80 °C to obtain an ointment in appearance, was bonded to 50% PTFE-loaded carbon papers and sintered at 350 °C for 30 min. Fig. 1 shows the transition electron microscopy (TEM) image of CNTs and scanning electron microscopy (SEM) image of carbon paper before and after immobilization of CNTs. TEM images were recorded by a Cs-corrected high-resolution TEM (JEM-2200FS, JEOL, Japan) operating at 200 kV, and SEM analysis was carried out on a Tescan VEGA device (Czech) after gold-plating of the samples.

The treatment experiments were performed in an undivided cell using a DC power supply (Micro, PW-4053S, Iran) with two electrodes. Fabricated carbon paper modified with CNTs with the geometric area of 40 cm^2 was used as cathode and a Pt sheet of 25 cm^2 area was employed as anode. The solution pH was measured by pH meter (WTW 720i, Germany) and adjusted by H_2SO_4. In all experiments, air was injected into the solution by an air pump at constant value for electrogeneration of H_2O_2 through Eq. (1). The UV-Vis spectra of solutions were obtained using a Hach UV-Vis spectrophotometer (DR 5000, USA) in the range of 190-800 nm. The concentration of each dye in treated mixture solutions was calculated after the UV-Vis data treatment using PLS method and color removal efficiency (CR (%)) was calculated through Eq. (4):

Table 1. The characteristics of three textile dyes

Dye	Chemical structure	Molecular formula	CAS No.	λ_{max} (nm)
RB69		$C_{23}H_{14}BrN_3O_9S\ Na_2$	59800-32-7	610
RR195		$C_{31}H_{19}ClN_7O_{19}S_6Na_5$	93050-79-4	542
RY84		$C_{50}H_{24}Cl_2N_{14}O_{30}S_{10}Na_{10}$	61951-85-7	408

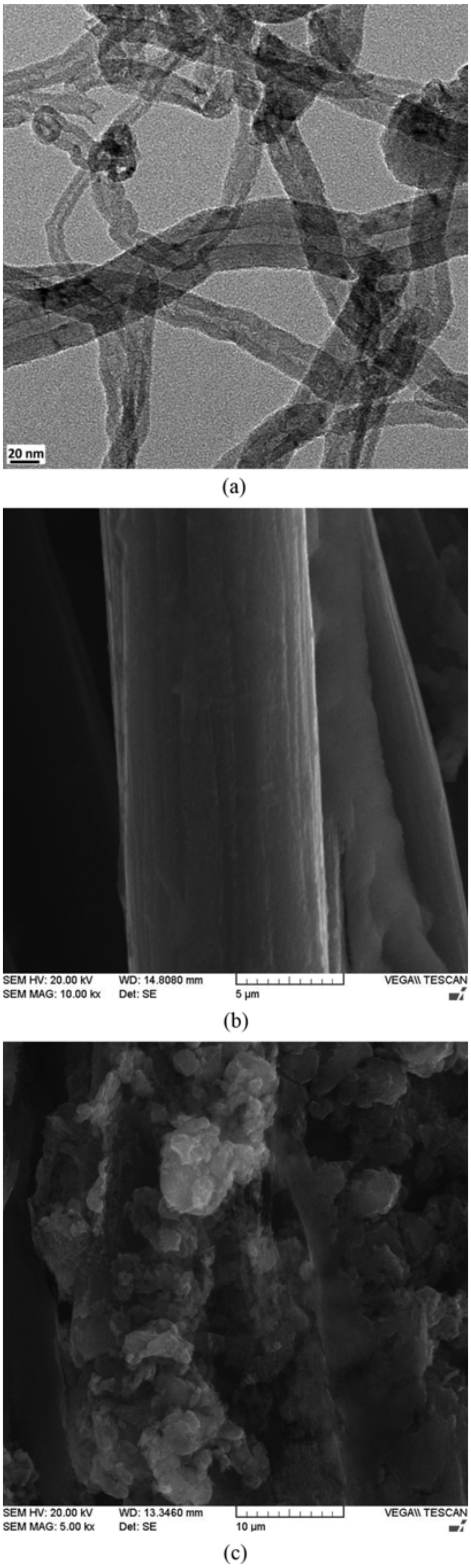


Fig. 1. (a) TEM image of CNTs; and SEM image of carbon paper (b) before and (c) after immobilization of CNTs.

Table 2. The ranges and levels of independent variables for experimental design

Variables	Ranges and levels				
	−2	−1	0	+1	+2
$[RY84]_0$ (mg/L) (X_1)	10	20	30	40	50
$[RR194]_0$ (mg/L) (X_2)	10	20	30	40	50
$[RB69]_0$ (mg/L) (X_3)	10	20	30	40	50
I (mA) (X_4)	100	200	300	400	500
Reaction time (min) (X_5)	40	80	120	160	200

$$\mathrm{CR}\ (\%) = \frac{C_0 - C}{C_0} \times 100 \tag{4}$$

where C_0 and C are the concentration (mg/L) before and after decolorization process, respectively. In each run, 250 mL of the three dye solution with initial concentrations designed by central composite design (CCD) containing 0.15 mM of Fe^{+3} ions and 0.05 M of Na_2SO_4 were decanted into the electrolytic cell. All the runs were performed at room temperature and solutions were stirred magnetically at a constant rate.

3. Experimental Design

In the present study, CCD as the most common form of RSM was used for the modeling and optimization of EF process for treatment of three dyes solutions. The influential factors for five-level CCD modeling were initial concentration of three dyes, applied current and reaction time. A total of 47 experiments were designed by CCD and performed including $2^5=32$ cube points, ten axial points and five replications at the center point. Experimental data were analyzed using Design Expert 7.0.0 software. The experimental ranges and the levels of independent variables for three dyes treatment are presented in Table 2. All PLS analyses were performed in MATLAB 7.12.0 (MathWorks, Natick, MA). Also, a free available graphical interface of multivariate calibration 1 (MVC1) was used [22].

RESULTS AND DISCUSSION

1. Comparison of Three Dyes Degradation by EF Process

The type and chemical structure of organic dyes has a considerable effect on the removal efficiency of these dyes in the electrochemical system. Since nearly 50-70% of the commercial and industrial dyes are azo compounds followed by the anthraquinone group, the degradation of mixture of two azo dyes, C. I. Reactive Red 195 (monoazo) and C. I. Reactive Yellow 84 (diazo), with one anthraquinone dye, C. I. Reactive Blue 69, has been investigated in this work. In the first section, to compare the color removal efficiency of these dyes, the decolorization of solutions containing 100 mg/L of each dye was investigated using EF process at a constant applied current, pH and Fe^{3+} concentration. The results are demonstrated in Fig. 2. As this figure shows, the electrochemical decolorization efficiency of RR195 was found to be higher than that of two other dyes. The three dyes have specified absorption in both ultraviolet and visible regions of the spectrum, so in this regard, the dyes are similar. The important structural difference between the three molecules is that in the case of RR195 and RY84 there is one and two azo groups (-N=N-), respectively, which is not present in RB69 molecule (see Table 1). This azo group is susceptible to degra-

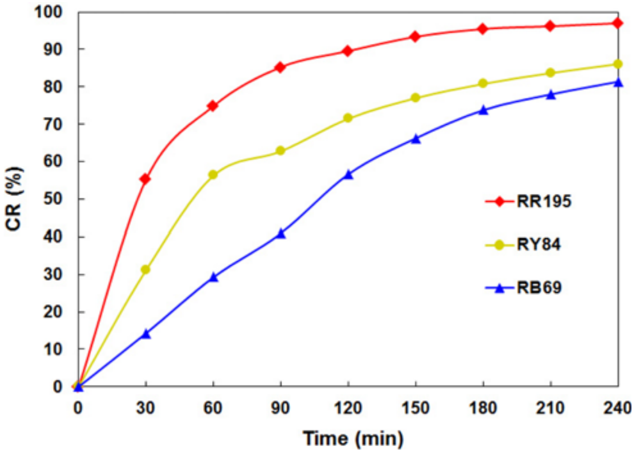


Fig. 2. Comparison of three dyes degradation by EF process; I=300 mA, [Fe^{3+}]=0.15 mM, [Na_2SO_4]=0.05 M, pH=3, [RR195]=[RY84]=[RB69]=100 mg/L.

dation by oxidative agents like $^{\bullet}OH$. Therefore, the first two dyes are degraded easily. In RB69, the presence of anthraquinone structure and the absence of azo bond make it resistant to degradation [23]. These main structural differences describe the observed order of the three dyes degradation (i.e., RR195>RY84>RB69). The anthraquinone group of organic dyes has a complex aromatic molecular structure which resists toward degradation in the environment and leads to remain colored for a long time. Some other studies have reported slower degradation of anthraquinone dyes compared to azo dyes [17,24-26].

2. Simultaneous Determination of Three Dyes by PLS Method

Fig. 3 shows the individual and mixture spectra of investigated three dyes. As is clear, due to the severe overlap of three dyes spectra, the usual univariate calibration method cannot be used to monitor the spectra of the three dyes in their mixtures. So, in these cases, multivariate spectrophotometric calibration methods such as PLS can be utilized for simultaneous determination of each dye in the presence of others. In this work, the PLS-1 mode of PLS regression was used. The cross-validation technique was applied to select the optimum number of factors. The details of this method have been reported in our previous works [2,27]. By utilizing this method for a validation set, the concentration of each sample was predicted and compared with known concentration of that sample and the predicted residual error sum of squares (PRESS) was obtained. The number of factors that made the least PRESS value was selected as the optimum number of factors [28]. The optimum number of factors for RY84, RR195 and RB69 dyes was obtained by applying mean-centered pre-processing algorithms to the spectra and are given in Table 3. The unknown interactions between the organic compounds in the mixtures cause a higher number of PLS-l factors than the number of components [29]. Other statistical parameters of cross-validation technique also are reported in Table 3 that indicate the ability of PLS-1 method for simultaneous determination of three dyes.

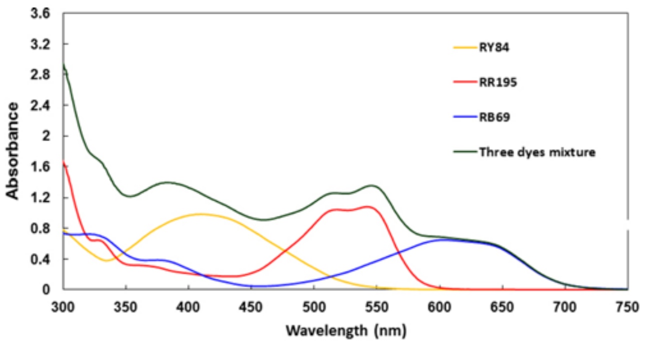


Fig. 3. The absorption spectra for three dyes (any dye concentration=100 mg/L and their mixture with the same concentrations).

Table 3. The statistical parameters of cross-validation process for PLS-1

Dye	ONF	PRESS	R^2	REP (%)
RY84	5	1.98	99.02	1.86
RR195	6	2.17	98.95	2.17
RB69	5	2.56	99.48	2.02

ONF: Optimum number of factors
PRESS: Prediction residual error sum of squares
R^2: Correlation coefficient obtained when plots of actual versus predicted concentration were constructed
REP: Relative error of prediction

After obtaining the optimum number of factors, the unknown set containing the spectra of samples treated by EF process was analyzed by PLS-1 method. Since the first-order multivariate calibration methods (e.g., PLS) are not able to analyze the absorbance data matrix in the presence of unknown compounds, the nature and chemical matrix of the calibration set should be similar to those of the unknown set. This similarity was verified by using augmentation of matrices method [2,30,31]. The achieved results for eigenvalues and chemical rank of calibration set, unknown set (spectra of mixture solutions treated by EF process) and an augmented matrix of them confirmed that no absorptive intermediate was produced during decolorization of three dyes. This revealed that the chemical composition of calibration and unknown sets was similar, and therefore, the PLS method is able to determine the concentration and color removal efficiency of each dye in the mixture solutions despite the overlap of their spectra.

3. Response Surface Modeling

In this study, 5-factor CCD with 47 runs was used to study the interactions between significant factors to optimize the decolorization efficiency of mixture of three dyes using EF process. Five replicates at the design center point were made to estimate the pure error of experiments. The designed 47 runs were done randomly to minimize the effect of unexplained variability on the responses due to systematic errors [32]. The ranges and levels of factors are presented in Table 2. The 5-factor CCD matrix and decolorization efficiencies obtained in EF process, after data analysis using PLS, are presented in Table 4. The second-order polynomial response equation (Eq. (5)) was used to correlate the color removal efficiency of three dyes as the dependent variable and the coded values of independent variables.

$$Y=\beta_0+\sum_{i=1}^{k}\beta_i X_i+\sum_{i=1}^{k}\beta_{ii}X_i^2+\sum_{1\le i\le j}^{k}\beta_{ij}X_iX_j \tag{5}$$

Table 4. The 5-factor CCD matrix and the value of response variable (CR (%))

Run	$[RY84]_0$ (mg/L)	$[RR195]_0$ (mg/L)	$[RB69]_0$ (mg/L)	I (mA)	Time (min	Color removal efficiency (%)					
						Experimental			Predicted		
						RY84	RR195	RB69	RY84	RR195	RB69
1	−1	−1	+1	+1	+1	78.01	96.21	61.12	79.52	95.88	62.70
2	−1	+1	−1	+1	−1	70.34	83.34	59.76	71.37	83.36	61.52
3	−1	−1	−1	−1	−1	70.21	86.76	58.23	70.24	85.38	58.39
4	−1	+1	+1	+1	+1	81.56	93.87	66.56	79.89	92.81	66.12
5	−1	−1	+1	+1	−1	70.76	89.34	58.09	71.42	91.68	56.59
6	−1	+1	−1	−1	−1	68.54	79.12	56.56	66.99	79.43	56.62
7	−2	0	0	0	0	86.09	91.43	68.83	83.50	92.35	66.45
8	+1	−1	−1	−1	−1	65.12	82.23	55.23	64.44	84.56	54.65
9	−1	−1	−1	+1	−1	76.23	91.11	61.11	73.74	89.43	60.60
10	+1	+1	−1	+1	−1	67.43	80.09	60.98	66.32	81.28	58.41
11	+1	−1	+1	−1	−1	59.43	86.67	51.12	60.12	84.06	49.64
12	+1	−1	−1	+1	−1	69.09	90.45	59.34	67.32	87.23	58.80
13	+1	−1	−1	−1	+1	75.02	93.32	65.65	74.67	93.38	65.20
14	−1	−1	−1	−1	+1	77.78	92.23	68.36	77.09	91.08	67.00
15	−1	+1	+1	−1	+1	71.86	87.12	60.69	73.27	87.38	61.72
16	+1	−1	+1	−1	+1	72.45	90.07	60.15	70.72	89.51	58.25
17	+1	+1	+1	+1	−1	67.32	81.11	54.91	65.74	81.53	56.27
18	0	0	0	+2	0	75.12	92.34	59.56	74.20	91.95	57.80
19	−1	+1	+1	−1	−1	66.32	86.76	58.90	65.67	83.18	55.36
20	−1	+1	−1	+1	+1	80.54	93.34	68.34	79.47	92.81	69.26
21	0	−2	0	0	0	75.90	96.23	61.76	74.70	95.85	61.35
22	0	0	0	0	0	73.45	91.00	59.57	73.32	90.54	59.69
23	−1	−1	−1	+1	+1	79.23	97.76	68.45	81.47	97.01	68.65
24	0	0	−2	0	0	73.12	90.12	75.87	74.90	90.15	73.60
25	−1	−1	+1	−1	−1	68.56	88.34	53.23	66.54	88.01	54.31
26	+1	+1	−1	+1	+1	78.76	94.23	69.57	77.79	93.86	68.09
27	+1	−1	−1	+1	+1	78.21	95.65	67.56	78.42	97.93	68.79
28	+1	+1	+1	−1	+1	71.34	85.09	59.12	71.59	86.68	57.67
29	0	+2	0	0	0	72.78	85.12	61.87	73.20	86.95	61.70
30	0	0	0	−2	0	63.34	82.32	47.34	64.70	83.85	49.25
31	0	0	0	0	0	73.65	91.67	59.11	73.32	90.54	59.69
32	0	0	+2	0	0	72.98	88.88	63.98	71.00	89.65	65.45
33	0	0	0	0	0	73.53	91.54	60.34	73.32	90.54	59.69
34	0	0	0	0	−2	50.56	73.87	41.22	54.10	75.45	43.85
35	−1	−1	+1	−1	+1	73.76	91.23	61.87	73.77	90.33	60.99
36	0	0	0	0	0	74.78	91.90	61.45	73.32	90.54	59.69
37	+1	+1	−1	−1	+1	74.11	92.32	59.65	73.17	89.43	61.81
38	0	0	0	0	0	74.32	90.56	60.23	73.32	90.54	59.69
39	+1	+1	+1	+1	+1	76.35	92.98	65.00	77.59	90.73	64.01
40	−1	+1	+1	+1	−1	71.65	89.11	62.65	71.42	86.73	60.32
41	+1	+1	+1	−1	−1	63.78	79.56	50.91	60.62	79.36	49.37
42	+2	0	0	0	0	72.21	89.12	58.34	75.40	89.45	60.60
43	−1	+1	−1	−1	+1	74.00	86.45	66.11	74.22	87.01	64.92
44	+1	−1	+1	+1	+1	76.32	94.87	62.56	75.84	93.68	61.90
45	0	0	0	0	+2	76.11	91.33	62.32	72.80	90.35	60.20
46	+1	−1	+1	+1	−1	65.23	87.11	55.11	64.37	86.36	53.85
47	+1	+1	−1	−1	−1	64.32	81.45	54.87	62.57	78.73	51.57

where, Y is the response variable (decolorization efficiency of each dye); X_i and X_j are independent variables; k is the number of variables (5 in our study); β_0 is the constant coefficient; β_i is the ith regression coefficient for linear effects; β_{ii} is the ith regression coefficient for squared effects and β_{ij} is the ijth regression coefficient for interaction effects. Based on the experimental results and after data analysis, the following second-order polynomial equations were obtained as an empirical relationship between the response and independent variables (see Eqs. (6)-(8)). These equations are the best fitted models after omitting insignificant terms based on the t-values and P-values. The significance of each factor in the regression model, which influences the response parameter (decolorization efficiency in this case), was determined by the larger t-values and smaller P-values (less than 0.05) [27,33,34].

RR195: $$Y=90.54-0.72\ X_1-2.22\ X_2-0.12\ X_3+2.02\ X_4+3.72\ X_5 -0.66\ X_4^2-1.91\ X_5^2-0.78\ X_1X_3+0.78\ X_1X_5+-0.84\ X_3X_5 \quad (6)$$

RY84: $$Y=73.32-2.02\ X_1-0.38\ X_2-0.98\ X_3+2.38\ X_4+4.68\ X_5 +1.53\ X_1^2-0.97\ X_4^2-2.47\ X_5^2+0.84\ X_1X_5 \quad (7)$$

RB69: $$Y=59.69-1.4625\ X_1+0.0875\ X_2-2.0375\ X_3+2.1375\ X_4 +4.0875\ X_5+0.9575\ X_1^2+2.4575\ X_3^2-1.5425\ X_4^2-1.9175\ X_5^2 +0.7031\ X_1X_3+0.6719\ X_1X_4 \quad (8)$$

The color removal efficiencies (CR (%)) of RR195, RY84 and RB69 were predicted by Eqs. (6)-(8) and presented in Table 4. These results show good agreement between experimental and predicted values of color removal efficiencies. This agreement and the quality of models can be evaluated by the determination coefficient (R^2) parameter. As can be seen in Table 4, the model predicted and experimental responses match well with R^2 values of 0.941, 0.925 and 0.938 for RY84, RR195 and RB69, respectively. These R^2 values indicate that more than 92% of variations in the response of each of three dyes can be explained by the obtained models. The value of adjusted R^2 (Adj-R^2) is also an estimate of goodness of fit and corrects the R^2 value for sample size and number of terms in the model, but it is more suitable for comparing models with different numbers of independent variables. The Adj-R^2 may be obviously smaller than R^2 if there are many terms in a model and not very large sample size [35]. In this study, Adj-R^2 values for RY84, RR195 and RB69 (0.895, 0.868 and 0.890, respectively) were very close to the corresponding R^2 values (see Table 5), which indicates the high significance of the models.

In addition to determination coefficients, the residuals (difference between the experimental and the predicted responses) are another tool for evaluating the adequacy of the models. The residuals are part of the variation unexplained by the suggested model and so should have a normal distribution. Fig. 4 shows normal probability plots of the residuals. In all three cases, the normal distribution of residuals indicates that the developed mathematical model is well fitted with experimental data.

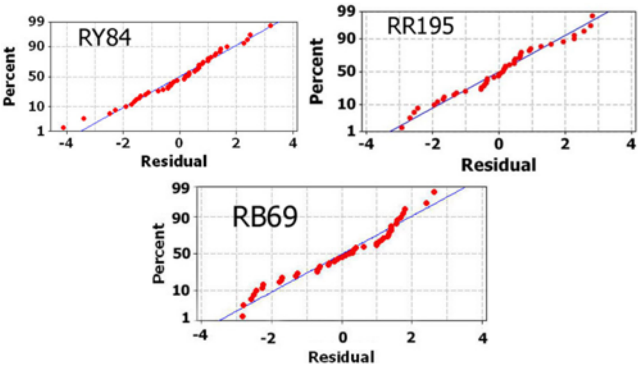


Fig. 4. Normal probability plots of residual for electrochemical color removal efficiency of three dyes.

The significance and adequacy of mathematical models and regression coefficients resulting from CCD was investigated by analysis of variance (ANOVA). The basic idea of ANOVA is a comparison of variation in the response variable associated with the model (change in the combination of variable levels) and variation associated with the random experimental error. This comparison is done by Fisher F-test (F-value), which is the ratio between the mean square of the model and the residual error [36]. The ANOVA results of response surface modeling in this study are summarized in Table 5. The F-values were 20.61, 16.13 and 19.64 for RY84, RR195 and RB69 models, respectively, which are obviously higher than the critical F-values (2.35 at 95% significance), confirming the adequacy of the fitted models.

4. Response Surface and Counter Plots

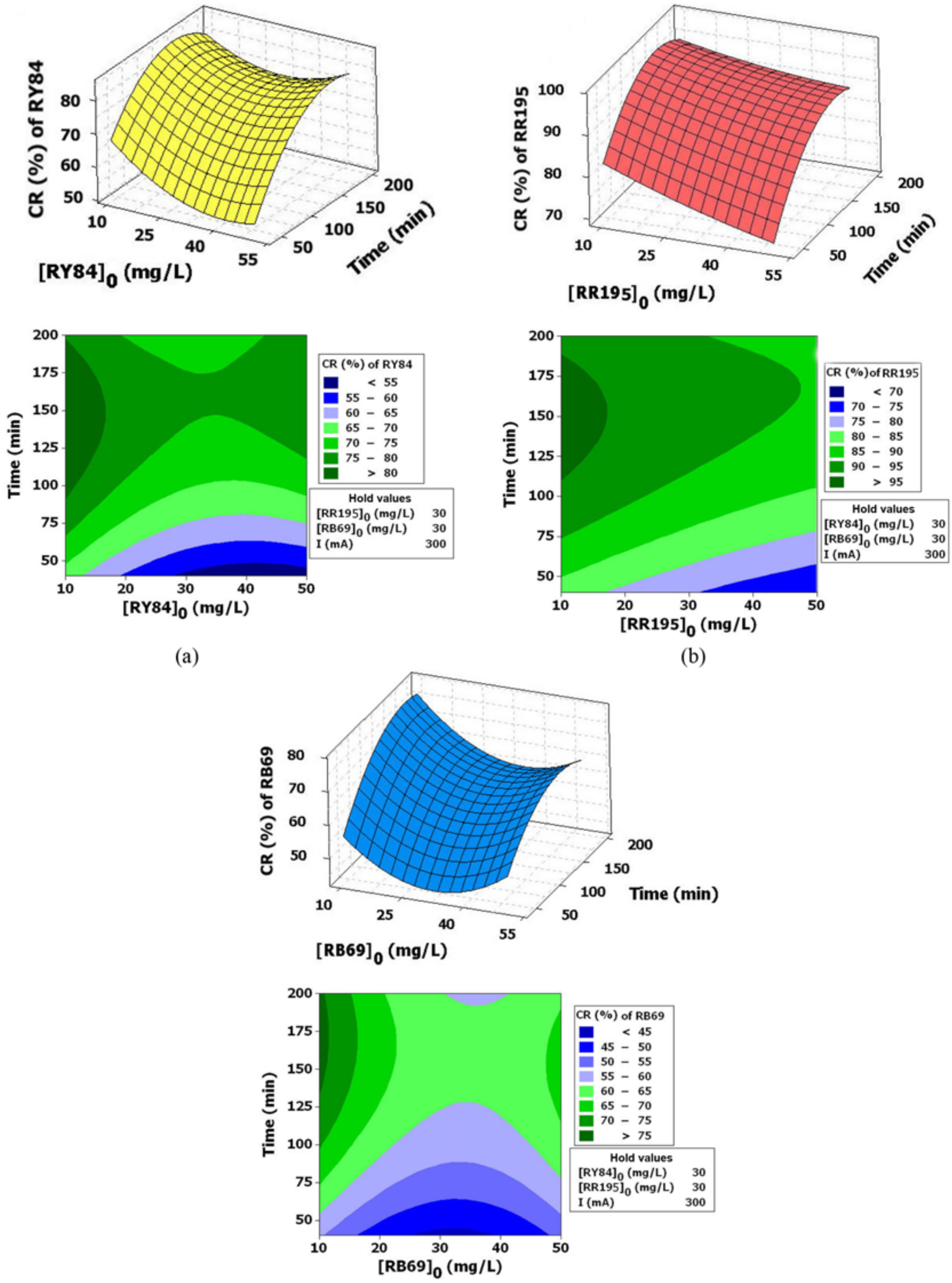
The effect of operational parameters on the color removal efficiency of three dyes is demonstrated as three-dimensional surface and two-dimensional contour plots. These graphical illustrations are the most useful tool to analyze the effect of each independent variable on the response. In the present study, response surface plots are useful for predicting the color removal efficiency for different values of operational parameters, and the type of interactions between these experimental variables can be investigated by using contour plots [37].

Fig. 5 shows the effect of initial dye concentration and reaction time on the color removal efficiency (CR (%)) in the EF process for each of three dyes. As can be seen, in all three cases, CR (%) decreases with increasing initial dye concentration. In the similar

Table 5. Analysis of variance (ANOVA) for fit of decolorization efficiency from CCD

Source of variations	Regression			Residuals			Total		
	RY84	RR195	RB69	RY84	RR195	RB69	RY84	RR195	RB69
Sum of squares	1648.47	1142.42	1584.55	103.96	92.05	104.86	1752.44	1234.48	1689.41
Adjusted mean square	82.42	57.12	79.23	3.99	3.54	4.03			
Degree of freedom	20	20	20	26	26	26	46	46	46
F-value	20.61	16.13	19.64						
P-value	<0.001	<0.001	<0.001						

RY84: R2=0.941, Adj−R2=0.895
RR195: R2=0.925, Adj−R2=0.868
RB69: R2=0.938, Adj−R2=0.890



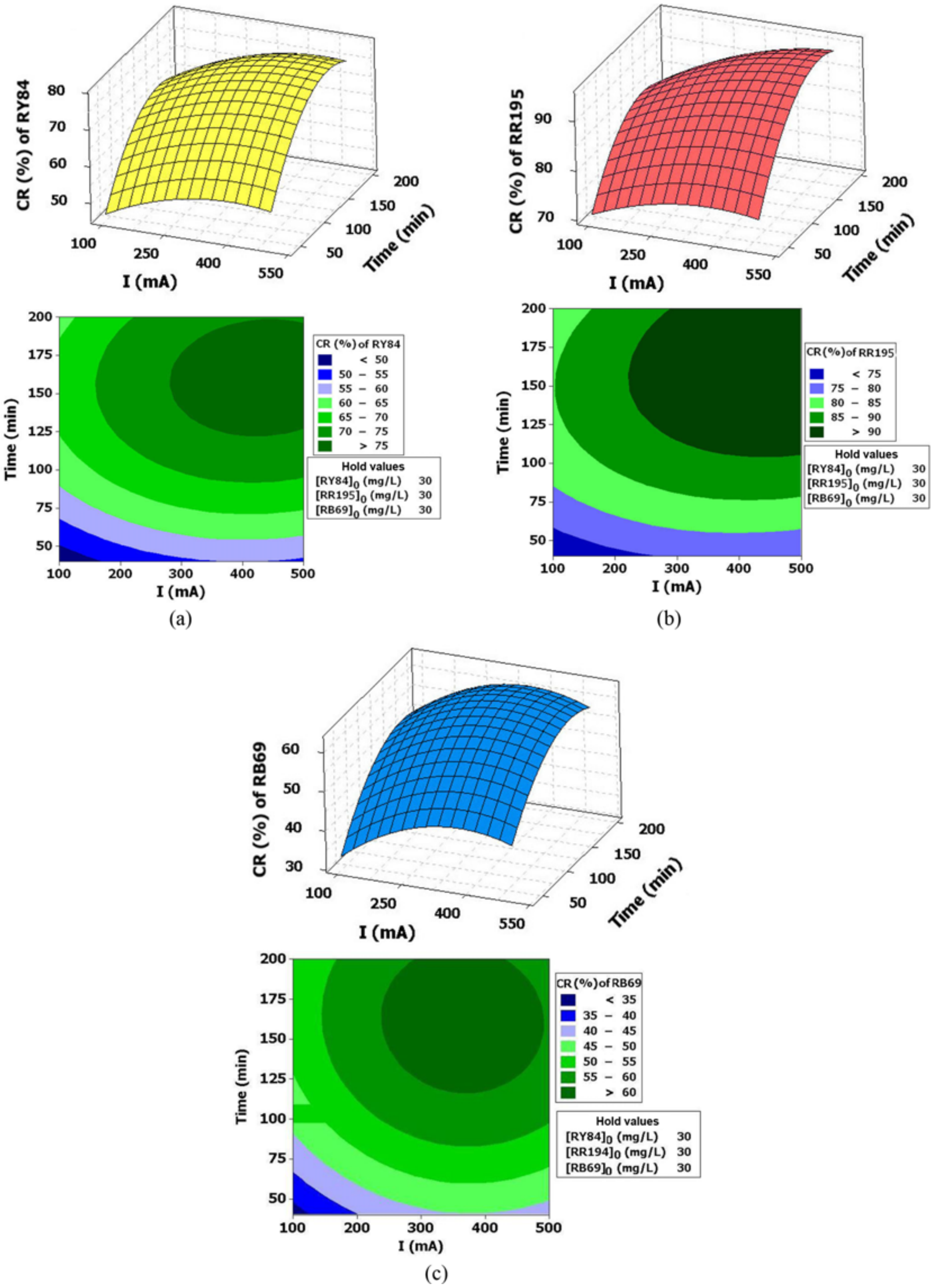
(a) (b)

(c)

Fig. 5. The response surface (3D) and contour (2D) plots of color removal efficiency as a function of initial dye concentration (mg/L) and reaction time (min) of (a) RY84, (b), RR195 and (c) RB69.

conditions of operational parameters of EF process (e.g., applied current, Fe^{3+} amount, pH, etc.), the same amount of oxidative agents like hydroxyl radicals is produced. When the pollutant concentration and, subsequently, their degradation intermediates and by-products are increased, the amount of available hydroxyl radicals is inadequate to react with these organics; thus, color removal efficiency is reduced [9]. Also, as it is obvious, the color removal efficiency increases with increasing reaction time; only, there is a slight decrease in the decolorization efficiency after 175 min of reaction for dye concentrations about 30-40 mg/L. But, since the general trend of AOPs (increase in the decolorization efficiency with time increasing) is clearly observed in these figures for all other concentrations, this insignificant decrease can be related to the negligible inability of PLS method for complete (100%) separation of three dyes concentration in the mixtures. This insignificant decrease in the color removal efficiency (less than 5%) can also be related to the experimental error.

Another important parameter in electrochemical processes like EF is the applied current served in the electrolysis system. Fig. 6 shows the response surface and contour plots of electrochemical decolorization efficiency as a function of applied current and reaction time. The CR (%) for each of three dyes increases with increasing the applied current up to 400 mA and after that, further increasing of the applied current up to 500 mA slightly decreases the decolorization efficiency. The increasing of CR (%) with increasing applied current can be related to the more generation of oxidizing species such as hydroxyl radicals (Eq. (2)) and hydrogen peroxide (Eq. (1)) in the solution. The negative effect of further increasing of applied



(a)

(b)

(c)

Fig. 6. The response surface (3D) contour (2D) plots of color removal efficiency as a function of applied current (mA) and reaction time (min) of (a) RY84, (b) RR195 and (c) RB69.

current indicates that the system has already reached its maximum oxidation power at about 400 mA. This negative effect can be described by using the cell potential. To employ the larger current values in the electrolysis system, a high voltage should be supplied; this high voltage leads to H_2O_2 decomposition either on the anode or in the medium directly (Eqs. (9)-(11)) [5,38].

$$H_2O_2 \rightarrow H_2O + 1/2\ O_2 \tag{9}$$

$$H_2O_2 \rightarrow HO_2^{\bullet} + H^+ + e^- \tag{10}$$

$$HO_2^{\bullet} \rightarrow O_2 + H^+ + e^- \tag{11}$$

CONCLUSIONS

The removal of mixture of three reactive dyes (C. I. Reactive Red 195, C. I. Reactive Yellow 84 and C. I. Reactive Blue 69) from aqueous solution has been studied by electro-Fenton process using carbon paper cathode modified with CNTs. Firstly, a comparison of three dyes decolorization was performed, and results showed that the color removal follows a decreasing order: RR195>RY84>RB69. Then, the partial least square and UV-Vis spectrophotometric method was used for simultaneous determination of three dyes during the electro-Fenton process. In this regard, five-level central composite design was used for the optimization of decolorization of the solution containing three dyes using the EF process. The factors for CCD modeling and optimization were the initial concentration of three dyes, applied current and reaction time in the EF process. Results indicated that the optimum applied current was about 400 mA for the decolorization process. Analysis of variance showed a high agreement between experimental and predicted responses with R^2 values of 0.941, 0.925 and 0.938 for RY84, RR195 and RB69, respectively. The effect of operational parameters on the color removal efficiency was evaluated by the response surface and counter plots of the model-predicted responses.

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REFERENCES

1. E. Brillas, E. Mur, R. Sauleda, L. Sànchez, J. Peral, X. Domènech and J. Casado, *Appl. Catal. B: Environ.*, **16**, 31 (1998).
2. A. R. Khataee, M. Safarpour, A. Naseri and M. Zarei, *J. Electroanal. Chem.*, **672**, 53 (2012).
3. S. Garcia-Segura, A. El-Ghenymy, F. Centellas, R. M. Rodríguez, C. Arias, J. A. Garrido, P. L. Cabot and E. Brillas, *J. Electroanal. Chem.*, **681**, 36 (2012).
4. P. Ghosh, L. K. Thakur, A. N. Samanta and S. Ray, *Korean J. Chem. Eng.*, **29**, 1203 (2012).
5. A. R. Khataee, M. Safarpour, M. Zarei and S. Aber, *J. Electroanal. Chem.*, **659**, 63 (2011).
6. N. Zhang, Y. Zhang and Y.-J. Xu, *Nanoscale*, **4**, 5792 (2012).
7. Y. Zhang, Z.-R. Tang, X. Fu and Y.-J. Xu, *ACS Nano*, **4**, 7303 (2010).
8. M. Zarei, A. Niaei, D. Salari and A. R. Khataee, *J. Hazard. Mater.*, **173**, 544 (2010).
9. A. R. Khataee, M. Zarei and R. Ordikhani-Seyedlar, *J. Mol. Catal. A: Chem.*, **338**, 84 (2011).
10. N. Djafarzadeh, M. Zarei, B. Behjati and A. R. Khataee, *Res. Chem. Intermed.*, **39**, 3355 (2013).
11. A. Ozcan, Y. Sahin, A. S. Koparal and M. A. Oturan, *J. Electroanal. Chem.*, **616**, 71 (2008).
12. M. Pimentel, N. Oturan, M. Dezotti and M. A. Oturan, *Appl. Catal. B: Environ.*, **83**, 140 (2008).
13. I. Sires, C. Arias, P. L. Cabot, F. Centellas, J. A. Garrido, R. M. Rodriguez and E. Brillas, *Chemosphere*, **66**, 1660 (2007).
14. S. Garcia-Segura and E. Brillas, *Water Res.*, **45**, 2975 (2011).
15. E. Brillas, I. Sires and M. A. Oturan, *Chem. Rev.*, **109**, 6570 (2009).
16. A. Özcan, Y. Sahin, A. S. Koparal and M. A. Oturan, *J. Hazard. Mater.*, **153**, 718 (2008).
17. A. Maleki, A. H. Mahvi, R. Ebrahimi and Y. Zandsalimi, *Korean J. Chem. Eng.*, **27**, 1805 (2010).
18. A. R. Khataee, A. B. Naseri, M. Zarei, M. Safarpour and L. Moradkhannejad, *Environ. Technol.*, **33**, 2305 (2012).
19. A. K. Gupta, A. Pal and C. Sahoo, *Dyes Pigments*, **69**, 224 (2006).
20. K. Sahel, N. Perol, F. Dappozze, M. Bouhent, Z. Derriche and C. Guillard, *J. Photochem. Photobiol. A: Chem.*, **212**, 107 (2010).
21. N. Djafarzadeh, A. R. Khataee, M. Khosravi and M. R. Sohrabi, *Fresenius Environ. Bull.*, **21**, 4022 (2012).
22. Http://www.Downloadplex.Com/scripts/matlab/development-tools/download-first-order-multivariate-calibration-scripts_349508.Html (accessed 2012.08.12).
23. A. R. Khataee and M. B. Kasiri, *J. Mol. Catal. A: Chem.*, **328**, 8 (2010).
24. M. B. Kasiri and A. R. Khataee, *Desalination*, **270**, 151 (2011).
25. B. Neppolian, H. C. Choi, S. Sakthivel, B. Arabindoo and V. Murugesan, *J. Hazard. Mater.*, **89**, 303 (2002).
26. M. A. Rauf and S. S. Ashraf, *Chem. Eng. J.*, **151**, 10 (2009).
27. A. R. Khataee, M. Safarpour and S. W. Joo, *Spectrochim. Acta, Part A*, **112**, 33 (2013).
28. L. An, J. Deng, L. Zhou, H. Li, F. Chen, H. Wang and Y. Liu, *J. Hazard. Mater.*, **175**, 883 (2010).
29. B. Hemmateenejad, M. Akhond and F. Samari, *Spectrochim. Acta, Part A*, **67**, 958 (2007).
30. R. Tauler, *Chemometrics Intellig. Lab. Syst.*, **30**, 133 (1995).
31. H. Wold, *Encyclopedia of the Statistical Sciences, Wiley*, **6**, 581 (1985).
32. R. H. Myers and D. C. Montgomery, *Response surface methodology*, Wiley, New York (2002).
33. K. P. Singh, S. Gupta, A. K. Singh and S. Sinha, *J. Hazard. Mater.*, **186**, 1462 (2011).
34. J.-C. Sin, S.-M. Lam and A. R. Mohamed, *Korean J. Chem. Eng.*, **28**, 84 (2011).
35. A. R. Khataee, M. Zarei, M. Fathinia and M. K. Jafari, *Desalination*, **268**, 126 (2011).
36. M. A. Bezerra, R. E. Santelli, E. P. Oliveira, L. S. Villar and L. A. Escaleira, *Talanta*, **76**, 965 (2008).
37. A. R. Khataee, M. Safarpour, M. Zarei and S. Aber, *J. Mol. Catal. A: Chem.*, **363-364**, 58 (2012).
38. M. Zarei, D. Salari, A. Niaei and A. Khataee, *Electrochim. Acta*, **54**, 6651 (2009).