Research Article

Spectrophotometric and kinetic studies on electro-chemical decolorization of dyes in mixtures: combination of classical least squares and hard modelling approaches

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In this study, kinetic electro-oxidations of four dyes were simultaneously evaluated on Ti/ ZnO-multi-walled carbon nanotubes anode. The mixture of dyes includes acid red 33 (AR33), reactive orange 7 (RO7), acid yellow 3 (AY3) and malachite green. The kinetic processes were monitored spectrophotometrically. A time-spectral data was analyzed in the time range 0 to 80 min and wavelength range of 220-700 nm which suffer signal overlapping of components problem.

To obtain the kinetic degradation profiles of the components, the whole data was resolved by classical least squares method as a reliable method for analysis of the data in which there are no selective responses for the analytes. Then, the kinetic rate constant of each dye decolorization together with its uncertainties were estimated by applying hard modelling approach. The obtained rate constants were 0.0675 s^{-1}, 0.0262 s^{-1}, 0.0168 s^{-1} and 0.0158 s^{-1} for MG, AR33, AY3 and RO, respectively, revealing that MG is the most degradable dye.

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1. Introduction

Water pollution as a crucial issue demands appropriate policy and techniques to prevent contamination of freshwater supplies and improve wastewater treatment. In the recent years, the growth of population and; industrial and agricultural expansion led to the excess rise in water consumption. The reports show there is wastewater discharge about 1500 km3 per year [1, 2]. The presence of synthetic compounds in effluent is really harmful to the environment and human health, even at trace level, and it is required to eliminate these pollutants before wastewater discharging.

Among a variety kind of synthetic dye-stuff, azo-dyes have a significant portion in effluents while they have the least desirable consequences towards surrounding ecosystems. These dyes are mainly resistant to aerobic degradation and they may produce carcinogenic aromatic amines in anaerobic conditions [3, 4].

Some conventional methods such as air stripping, extraction, ultrafiltration, carbon adsorption have been employed for the removal of azo-dyes from wastewater. However, these techniques are non-destructive and they commonly transfer the pollutants from one phase to the other one without decomposing them [5, 6]. In recent years, advanced oxidation processes (AOPs) have gained widespread applications in degrading industrial wastewater due to their ability for decomposing dyes in aqueous solutions [7- 9]. Among AOPs, electrochemical advanced oxidation processes (EAOPs) are highly applicable for eliminating the dyes and oxidizing them during the removal processes. These methods possess some advantageous such as cost-effectiveness, environmental friendliness, simplicity of operation, high removal efficiency and preventing secondary wastewater treatment [8,10].

The efficiency of EAOPs is greatly depends on the anode material because electrochemical oxidation (EO) reactions occur between the electrode surface and solution especially production of °OH; therefore, the selection of the proper anode is a key factor in the remediation of dye-containing wastewater. In 2022, Mahmoudian et. Al. fabricated titanium electrode coated with nanocomposite of ZnO-multi-walled carbon nanotubes (ZnO-MWCNTs) by electrophoretic deposition (EPD) method and applied it for remediation of water solution contained different dyes including Acid red 33 (AR33), Reactive orange 7 (RO7), Acid yellow 3 (AY3) and Malachite green (MG) [8]. They investigated the performance of the constructed Ti/nanoZnO-MWCNTs electrode in the EO processes of these dyes in a mixture, as a target for wastewater. They monitored the EO reactions using cost-effective and simple spectrophotometric technique where the analysis of the data was impossible using univariate techniques due to the signal overlapping of the dyes. To overcome this problem, they proposed a multivariate calibration technique to find the concentration of each dye at the final time of decolorization process.

EAOPs are kinetic processes intrinsically and the reaction rate constants of decolonization reactions permit a chemist /chemical engineer to design, operate, control and optimize the reactors of the chemical industries. For instance, it could be checked if the process is in or out of control. A kinetic process can be monitored spectroscopically and there are special multivariate resolution methods developed to estimate reaction rate constants and underlying spectra [11-15]. Although the most wastewaters are composed of different contaminants, in our best of knowledge, there is no report on the determination of simultaneous EOs rate constants of several dyes with severely overlapped signals and it is a neglected issue in EOAPs systems.

Multivariate analysis has been widely applied for monitoring chemical processes such as kinetic and equilibrium systems and provide a better understanding of the system under study with saving in cost and time. In this regard, spectrophotometric method is one the most common technique providing multivariate data which can be analyzed by suitable multivariate algorithms. Although, it shows spectral overlapping and non-specific signal for the analytes in mixtures, it can be analyzed successfully by multivariate chemometrics methods as promising and powerful techniques

This work deals with the above-mentioned neglected issue in EOAPs. The decolorization reactions in an aqueous mixture containing several dyes, studied by Mahmoudian et al, were selected as model of EOAPs system. The dyes include AR33, RO7, AY3 and MG showing strongly overlap signals where the processes monitored spectrophotometrically. It will be shown how combination of classical least square method [16] and hard-modelling technique [11,12] can help researchers achieve the kinetic profiles and rate constants of the dyes decolonization simultaneously.

2. Experimental
Electrochemical oxidation of the dyes Procedure

Batch electrolytic cell reported in [8] was applied in this study to conduct electrochemical oxidation of the dyes. A mixture of the dyes was prepared in a 250 ml cylindrical glass reactor, in which the concentrations of dyes were 25, 25, 10 and 10 mgL^{-1} for AR33, RO7, AY3 and MG, respectively. The anode and cathode electrodes were Ti/nanoZnO-MWCNT electrode and stainless-steel plate (dimensions: 3×3 cm; thickness: 1 mm), the solution was stirred throughout the experiment to make an efficient mass transfer in the experiment. To monitor the decolorization process, 3ml of the sample was withdrawn from the cell at a given time and its spectrum was obtained using UV–Visible spectrophotometer with 0.5 nm interval in the wavelength range of 200–800 nm. It was observed that the signals at the wavelength more than 700nm were not significant; moreover, there were no significant changes of signals at the wavelength less than 220 nm. Therefore, the data was selected in the range of wavelength 220-700 nm for further analysis. Indeed, a two-way data was obtained at 966 wavelengths, 12 electro-oxidation times from 0 to 80 min where no significant changes observed in the signals.

3. Theory

3.1. Classical Least Squares

The intentional objective in chemical systems is commonly the assessment of concentrations of individual components (**C**) or the recognition of unknown spectral profiles (**S**) in mixture solutions. CLS model has the capability to calculate each **C** when **S** is known or vice versa**.** This strategy is stood on the following matrix equation:

$$\boldsymbol{X} = \boldsymbol{C} \times \boldsymbol{S^T} + \boldsymbol{R} \tag{1}$$

Where **X** is the prime raw data matrix with the mixed experimental information, that way; the columns in **C** and their corresponding rows in **S**^{T} consist of pure concentration and spectral profiles of the components involved in the data **X**, respectively, and **R** is the residual matrix. When the pure spectral components are known, matrix **C** can be obtained based on the least squares minimization of $\|\boldsymbol{R}\|$**,** written as follows [16]:

$$\mathbf{C} = \mathbf{X}(\mathbf{S}^T)^+ \tag{2}$$

Where the sizes of the relevant matrices are **X** (I×J), **C** (I×N), **S** (J×N), and **E** (I× *J*); and I*,* J*,* and *N* are the number of degradation times, wavelengths, and spectroscopically active components, respectively.

3.2. Hard-Modelling Technique

Hard-modelling method is an iterative process and calculates the best set of independent parameters in a defined model based on a least-squares algorithm. In this method, the goal is minimizing the sum of squares (SSQ) which is a function of a chemical model and its parameters [11, 12]:

$$SSQ= \sum_{i=1}^{i=m} \sum_{j=1}^{i=n}(R_{i,j}^2)=f\ (\textbf{C, model, parameters}) \qquad (3)$$

The parameters are linear and non-linear attributed to the elementds of each column vector in matrix **C** and kinetic constants involved in matrix **C**, respectively. It should be mentioned that the linear parameters can efficiently be eliminated during iteration process. Indeed, hard modeling strategy is a robust analysis technique because it fits few number of parameters, i.e., non-linear ones. In this work *lsqnonlin* Matlab command, based on Newton-Gauss Levenberg Marquardt (NG/LM) algorithm, is used to conduct fitting. During the optimization, the concentration profiles of species are calculated by first-order kinetic equations. Indeed, many chemical processes are of a first-order nature or can be at least experimentally observed under pseudo-first-order conditions in which estimating the rate constants are not dependent on initial concentrations [14, 15].

4. Results and Discussion

The time-spectral data of electrochemical oxidation of synthetic dyes mixture was depicted in Fig 1. To achieve the pure spectral profiles of the dyes, the standard solution of each dye (40ppm) was prepared and its spectrum was recorded using Uv-vis spectrophotometer at the same wavelength range in the electro-oxidation processes' monitoring. It should be noted that these obtained spectra are the same as their corresponding pure profiles in the shape but different in intensity.
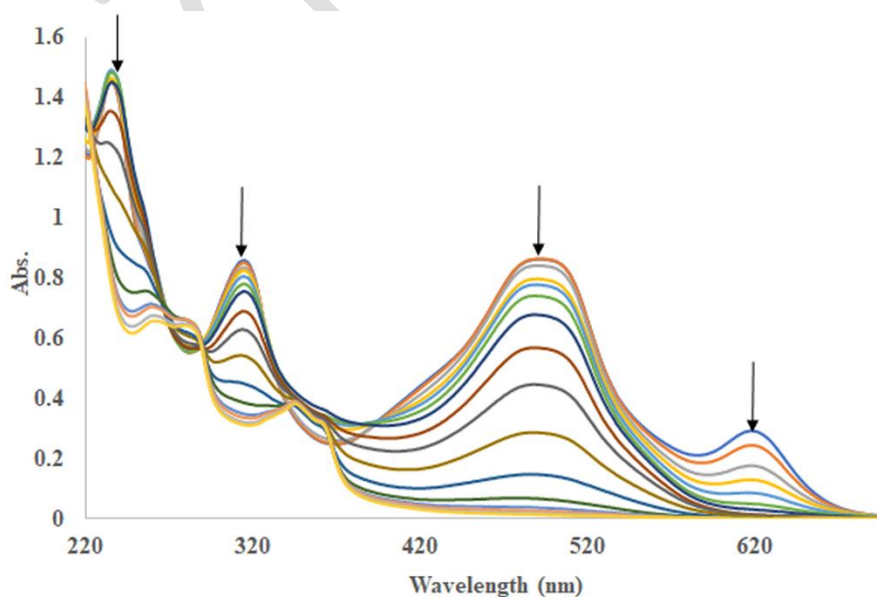

Fig 1. Time-spectral data of in synthetic mixtures of dyes containing AR33 (25 mgL⁻¹), RO7 (25 mgL⁻¹), AY3 (10 mgL⁻¹) and MG (10 mgL⁻¹)

Given that, in the first-order reaction, the rate constant of the kinetic process can be estimated when the initial concentration of analyte is unknown, all the recorded spectra of standard solutions were normalized as illustrated in Fig. 2. Then CLS model was applied on the data under these normalized pure spectral profiles (**S** in Eq. 2) to obtain the kinetic profiles of the components; however, the profiles were not reliable, for example, there were not unimodal or some of their values were negative, as we know, negative value for the concentration of a component is vague.
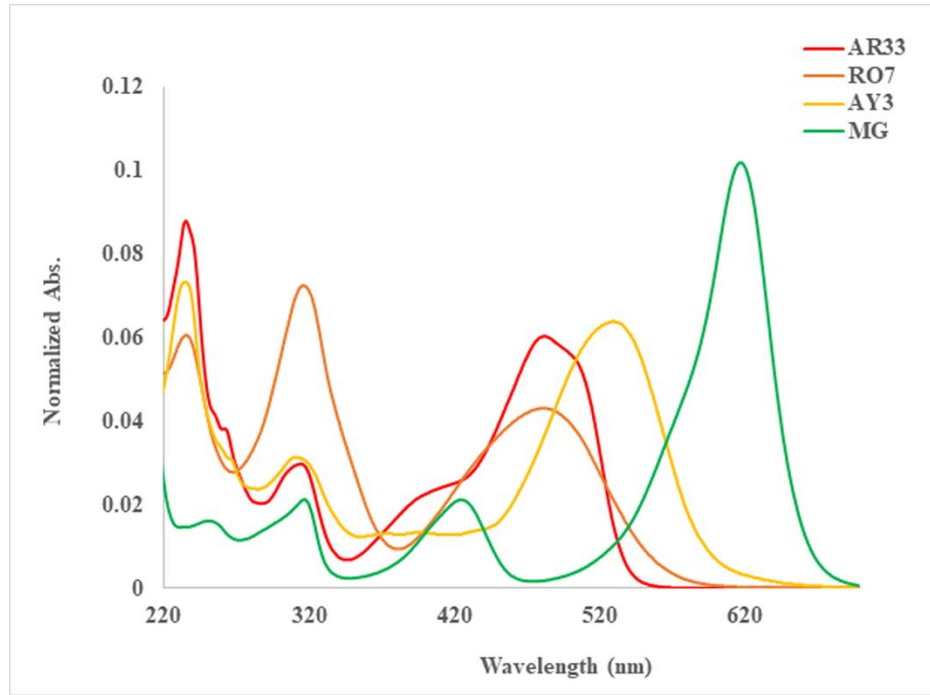

Fig 2. Normalized pure spectral profiles of the dyes

As seen in Fig. 1, the signals of the components are severely overlapped in the wavelength range of 220-400 nm and this part of data possesses low information due to the lack of selectivity. Thus, we omitted this part from the data and pure spectral profiles and then CLS model was employed on the remained data under the normalized pure spectral profiles. The obtained concentration profiles have been illustrated in Fig 3. To evaluate the ability of CLS analysis, the standard deviation of residuals of data analysis (s_{cls}) was computed based on the following equation:

$$s_{cls} = \sqrt{\frac{\sum_{i=1}^{I}\sum_{j=1}^{J} R_{ij}^2}{I \times J - (N \times J)}} \tag{4}$$

Where, R_{ij} is the element of residual matrix **R**; and I, J and N are the same as in equation 2.
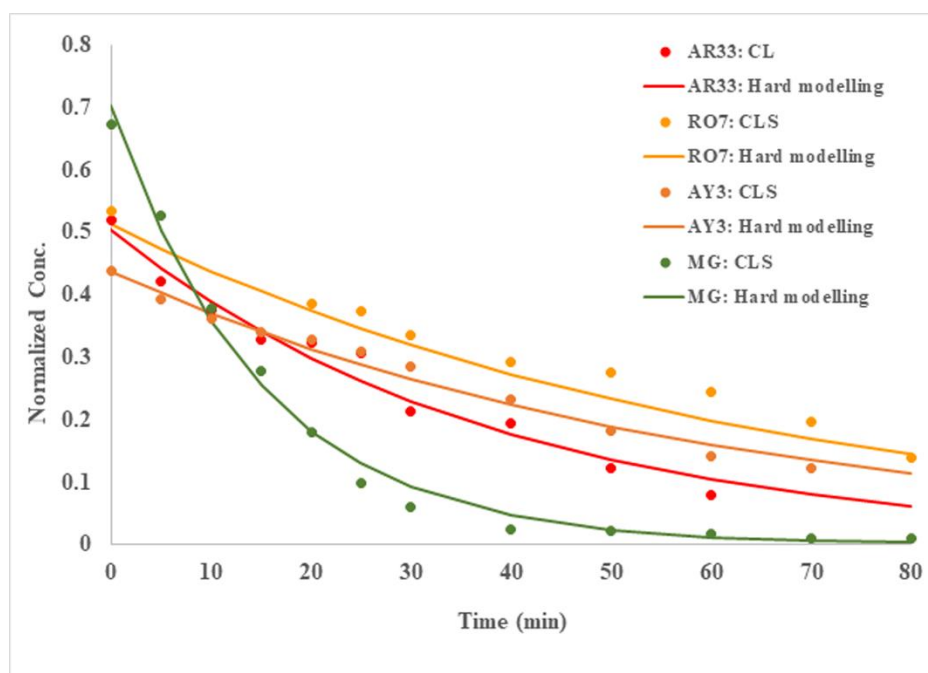
Fig3. Normalized concentration profiles of the dyes obtained by CLS method (Paint) and hard modelling

approach (Solid line)

The calculated s_{cls} was 0.0173 which confirms the unmodelled part of data is attributed to the noise. To compute the rate constant of each dye decolorization (k), each kinetic profile was analyzed by hard modelling approach based on postulated first-order reaction $A \xrightarrow{k} B$ as follows:

$$A_t = exp(-kt) \qquad\qquad (5)$$

Where the initial substrate is one, A_t is the concentration of the dye involved in a first-order reaction at electro-oxidation time t and k is the rate constant of the decolorization. Fig. 3 overlays the obtained normalized concentration profiles by CLS method and their corresponding fitted profiles by hard modeling approach. This figure reveals that the obtained normalized concentration profiles by CLS method match well with those of hard modeling approach. The estimated k*s* together with their corresponding standard deviations have been reported in Table 1. This table compares the rate constants of degradation processes of the dyes and shows that MG is the most degradable component in this system as its rate constant is significantly high. It seems the structure of the dye molecule could be responsible for the degradation mechanism.

Table 1. The estimated decolorization rate constants of the dyes by hard modeling method

Dyes	k (min^{-1})
AR33	0.0262 ($\pm$0.002)
RO7	0.0158 ($\pm 4.95 \times 10^{-4}$)
AY3	0.0168 ($\pm 8.94 \times 10^{-4}$)
MG	0.0675 ($\pm$0.0034)

5. Conclusion

The main focus of this work is kinetic studying of the electrochemical oxidation degradation of synthetic dyes mixture composed of AR33, RO7, AY3 and MG on Ti/nanoZnO-MWCNTs electrode at the optimal operational parameters including pH, current, electrolyte concentration with values , respectively These simultaneous kinetic processes were monitored spectrophotometrically at wavelength range of 400-700 nm where the signals of the components are highly overlapped as it was not possible to obtain the kinetic profiles of the analytes . Here, classical least square method was proposed to overcome this problem. Indeed, multivariate analysis technique allows me to obtain the pure kinetic profiles of degraded dye, all of which are the same as real pure profiles in shape but different in intensity.

To estimate the kinetic rate constant (k) of degradation processes, the concentration profile of each component was fitted by hard modelling approached based on NG/LM algorithm which computes both the k and its standard deviation. ks values were 0.0675 s^{-1}, 0.0262 s^{-1}, 0.0168 s^{-1} and 0.0158 s^{-1} for MG, AR33, AY3 and RO7, respectively, revealing that MG is the most degradable dye.

Conflicts of Interest

The author declares that there is no conflict of interest regarding the publication of this article.

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