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Kinetic and residence time distribution modeling of tubular electrochemical reactor: analysis of results using Taguchi method

R. Mythilishri, V. P. Kamalakannan, R. Saravanathamizhan* and N. Balasubramanian

Department of Chemical Engineering, A.C. Tech Campus, Anna University, Chennai 600025, India

*Corresponding author. E-mail: thamizhan79@rediffmail.com

Abstract

Decolorization of dye waste water is performed using a tubular electrochemical reactor. Stainless steel and oxide coated on titanium mesh acts as the cathode and anode respectively. Experiments were conducted in batch with recirculation mode. The effect of operating parameters such as current density, initial dye concentration, flow rate and supporting electrolyte concentration on decolorization of Acid red dye has been studied and the results were analysed using Taguchi method. A residence time distribution (RTD) study has been conducted in a tubular electrochemical reactor and an axial dispersion model has been developed to determine percentage decolorization. The model results are compared with experimental results and it was found that the model satisfactorily matches with the experimental results with high correlation coefficient.

Key words: axial dispersion model, dye waste water, electrochemical reactor, RTD modeling, Taguchi method

INTRODUCTION

Treatment of effluent is a global concern. Dye wastewater from the textile industry can pose a serious threat to the environment and it is difficult to decolorize because of its structural complexity. Most of the azo dyes are carcinogenic and affect the marine ecosystem and generally they contain two or more aromatic rings joined by one or more azo groups. Acid red is classified as a single azo dye, which is used in the textile industry especially for nylon, cotton and wool. The dye adds harmful organic matter to the aquatic environment (Ayman *et al.* 2019). Chemical and biological treatment methods such as coagulation, adsorption, ion exchange, coagulation-flocculation, activated sludge process, and anaerobic-aerobics have been used for treatment. However, these treatment techniques have some disadvantages like requirement of huge amounts of chemicals, secondary treatment to further remove the sludge formed from the primary treatment, demand for large area and the sensitivity of microorganisms. Frequent clogging and membrane fouling is a major issue in separation techniques. The electrochemical process is a better solution to overcome the limitations of chemical and biological treatment. Recently, researchers have been focusing on the electro-oxidation technique. In electrooxidation, electrons are the main reagent and mineralization of organic pollutants is achieved (Nideesh *et al.* 2018). It is also reported that electro-oxidation achieved maximum color removal efficiency (Kaur *et al.* 2017).

In electrochemical reactors, kinetic modeling and residence time distribution (RTD) studies has been conducted by many researchers. Kinetic study has been attempted in electrochemical reactors for different modes of operation and various types of reactors. Soloman *et al.* (2009b) studied different modes of operation using RuOx–IrOx–TiOx coated titanium for removal of organics from agro-based paper industry using a tubular electrochemical reactor. Singh *et al.* (2016) investigated electro-oxidation of malachite green dye using RuO_2–TiO_2 and Pt-coated Ti mesh electrode. Santos *et al.* (2018) studied the removal of Acid red 1 dye using Ti/TiO_2-nanotubes/PbO_2. The authors observed

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that Ti/TiO_2-nanotubes/PbO_2 anode performs better than Ti/TiO_2 for the removal of Acid red 1 dye. Ibrahim *et al.* (2013a) carried out experiments in a batch, stack and cylindrical electrochemical cell for simultaneous chemical oxygen demand (COD) reduction in the dye effluent. The authors reported that the degradation rate is affected by the electrolyte flow in the cylindrical cell compared to the tank cell and batch cell. Ibrahima *et al.* (2014) performed the treatment of petroleum effluent using electrochemical tubular reactor. They have achieved 85% COD reduction using ruthenium oxide coated titanium anode. Oukili & Loukili (2019) performed the degradation of textile azo dye Methyl Orange a cylindrical platinized titanium (Ti/Pt) grid as anode. The author reported that 98.51% of color removal was achieved.

Literature also shows electrochemical reactor of flow visualization using computational fluid dynamics (CFD) and RTD studies. Saravanathamizhan *et al.* (2008) proposed a Tanks-in-series model for the electrolyte flow behavior in a continuous stirred tank electrochemical reactor and the model is verified using RTD study. Martínez-Delgadillo *et al.* (2010) investigated the performance of the tubular electrochemical reactor with different inlets; that is, central, lateral and tangential. The author reported that tangential inlet gives homogenous axial velocity and the degree of back mixing is reduced significantly. Ibrahim *et al.* (2013b) studied flow dynamics and mass transfer in a tubular electrochemical reactor using RTD and CFD were used to analyze the flow dynamics inside the reactor. It is reported that the presence of dead volume, bypass and short circuiting decreases with increase in flow rate.

The RTD analysis of a vessel gives useful information on flow characterization. The RTD study shows how long the fluid element stays inside a reactor, as a quantitative measure of the degree of back mixing within a system. The knowledge on RTD is important to determine the conversion of the fluid inside the reactor for the first order kinetics, which helps with reactor design (Fogler 1999; Levenspiel 1999).

The literatures have reported kinetic modeling, electro oxidation analysis using statistical analysis, flow modeling using CFD and RTD. The present research focuses on kinetic modeling and residence time distribution modeling for the cylindrical flow electrochemical reactor. Based on the information obtained from the RTD, the decolorization of synthetic dye wastewater was estimated for the electro oxidation using a tubular electrochemical reactor.

MATERIALS AND METHODS

Chemicals

The synthetic dye effluent is prepared using Acid red 87 dyes. The structure of the dye is shown in Figure 1. Sodium chloride is used as the supporting electrolyte.

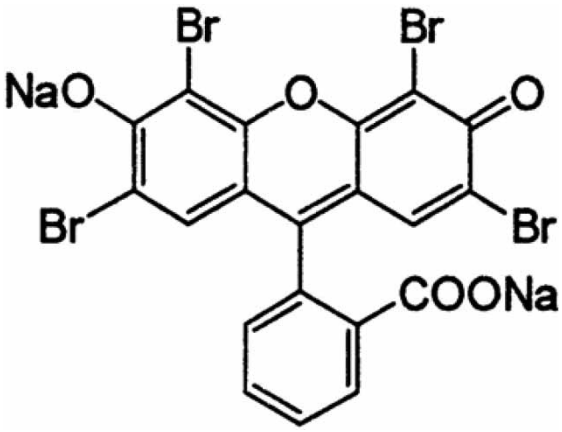

Figure 1 | Molecular structure of Acid red 87 dye.

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Experimental

The experimental setup of the tubular reactor is shown in Figure 2. The reactor consists of a cylindrical shaped cathode and mesh type anode, storage tank to store dye wastewater, circulation pump and regulated power supply. The reactor is 7 cm in diameter, 110 cm high and made of stainless steel that acts that as the cathode and inside the reactor mesh type anode $Ti/Ti_{0.7}Ru_{0.3}O_2$ of 5 cm diameter, 100 cm height is inserted and sealed with end frames. Electrodes are connected to the regulated power supply (100A, 0–50 V). Mesh type anode having 60% perforation have an effective anode area of 628.3 cm^2. All the connections are made using silicone rubber tubes. For the decolorization experiment, three different dye concentrations of 100, 200 and 300 mg L^{-1} are taken with the recirculation flow rate of 30, 60 and 90 LPH. Current density and supporting electrolyte also varied as 6, 9 12 mA cm^{-2} and 1, 2, 3 g L^{-1} respectively. In the present work, a batch with recirculation operation was performed to study the dye decolorization and once through mode was used to study RTD.

Taguchi design

Taguchi method is one of the statistical analyses, based on orthogonal arrays, the experimental design was developed. MINITAB software tool was used to develop the experimental design. Four variables of dye concentration (A) flow rate (B) current density (C) and supporting electrolyte concentration (D)

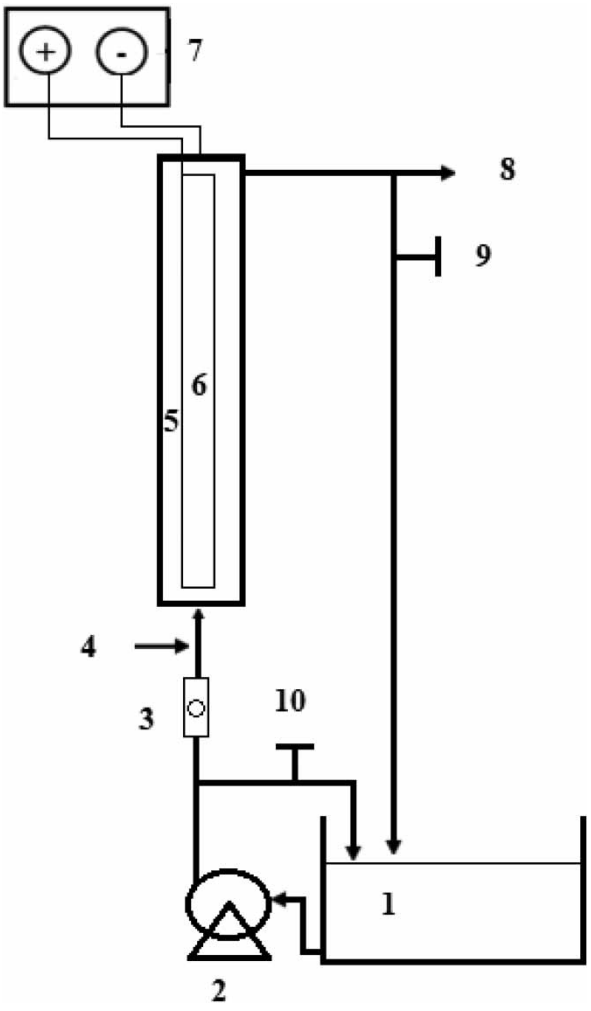

Figure 2 | Schematic representation of electrochemical reactor. 1 Reservoir, 2 pump, 3 rotameter, 4 tracer injection point, 5 stainless steel cathode, 6 oxide coated mesh type anode, 7 DC power supply, 8 reactor outlet, 9,10 control valve.

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are selected at three different levels shown in Table 1. The three level and operating parameters were selected based on preliminary experiments. The experimental color removal is observed as output response. A suitable orthogonal array design table (Table 2) is designed and the selection based on the number of variables and number of levels is shown in Table 1. Taguchi method, S/N ratio is used to identify the optimum condition of the experiment.

The S/N ratio characteristics are divided into three steps: the smaller the better, nominal is the best, and the larger the better (Ghani *et al.* 2004; Davila *et al.* 2011; Nandhini *et al.* 2014). Taguchi method S/N ratio calculation according to the 'larger-the-better' was calculated as follows:

$$\frac{S}{N} = -10\log\frac{1}{n}\sum\frac{1}{y^2} \tag{1}$$

where n is the number of observations, and y is the observed data. For the present experiment, larger color removal is better hence a higher S/N ratio is better for result.

Table 1 | Variables and their values corresponding to their levels investigated in the experiments

Variables		Unit	Level		
			1	2	3
A	Dye concentration	mg L^{-1}	100	200	300
B	Flow rate	LPH	30	60	90
C	Current density	$mAcm^{-2}$	6	9	12
D	Supporting electrolyte concentration	g L^{-1}	1	2	3

Table 2 | Experimental variables, their levels and results of conducted experiments corresponding to L9 experimental plan

S. no.	A	B	C	D	Color removal (%)
1	100	30	6	1	36.32
2	100	60	9	2	91.05
3	100	90	12	3	99.09
4	200	30	9	3	65.08
5	200	60	12	1	53.79
6	200	90	6	2	40.92
7	300	30	12	2	50.72
8	300	60	6	3	29.99
9	300	90	9	1	40.45

Residence time distribution study

Pulse input of the tracer experiments were conducted for the residence time distribution study in the same experimental setup shown in Figure 2. For RTD studies, the tubular reactor was operated with water as the electrolyte fluid in once-through mode. Acid red dye solution is a tracer, was injected and samples were collected periodically in different time intervals at the outlet of the electrochemical reactor. The water was circulated at different flow rates without electro-oxidation. The samples were analyzed using a UV spectrophotometer. The E(t) can be calculated from tracer output using

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the following equation (Fogler 1999; Levenspiel 1999).

$$E(t) = \frac{c(t)}{\int_0^\infty c(t)dt} \tag{2}$$

where c(t) represents the exit tracer concentration at time 't'. The mean residence time can be calculated as

$$\tau = \int_0^\infty tE(t)dt \tag{3}$$

The variance for CSTER can be written as

$$\sigma^2 = \int_0^\infty (t-\tau)^2 E(t)dt \tag{4}$$

RESULT AND DISCUSSION

Kinetic modeling

The kinetics of electro-oxidation of dye wastewater for different flow rates is shown in the Figure 3. The reservoir is assumed to be a completely mixed tank and the flow to the tubular reactor is assumed to be a plug flow. The reaction rate for the decolorization in a batch reactor with recirculation under steady state can be given as (Soloman *et al.* 2009a; Vijayakumar *et al.* 2016):

$$\frac{C}{C_o} = \exp\left\{-\frac{t}{\tau}\left[1-\exp\left(-k_h\frac{A_e}{Q}\right)\right]\right\} \tag{5}$$

where τ is the residence time in the reservoir (V_r/Q). The heterogeneous rate constant k_h can be calculated from the plot $-ln(C/C_o)$ vs. t having the slope $((1-\exp(-k_hA_e/Q))/\tau)$. Figure 3 shows the kinetics

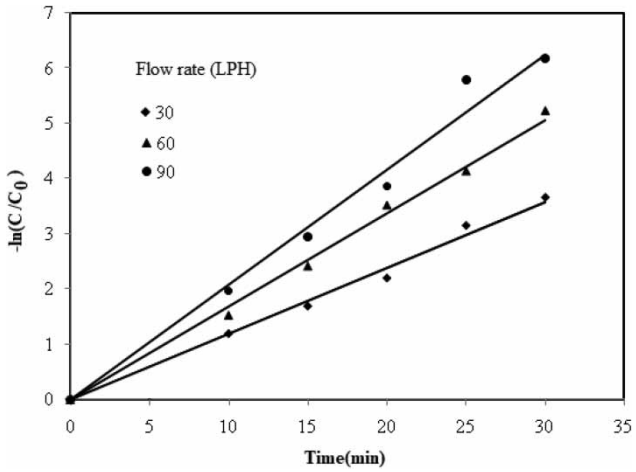

Figure 3 | Kinetics plot of $-ln(C/C_o)$ vs. t for the batch with recirculation operation of a tubular electrochemical reactor. Current density 12 mA/cm^2; initial concentration 100 mg L^{-1}.

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plot of the batch recirculation electrochemical reactor. The rate constant varies from 4.69×10^{-3} to 5.87×10^{-3} cm s^{-1} with increasing dye flow rate. Increase of rate constant at higher flow rates is due to increasing enhancement of mass transfer and decreasing resistance on the surface of the electrode.

Taguchi analysis

The mean value of acid red 87 dye color removal using electro oxidation is shown in Figure 4. The mean value plot is used to understand the effect of variables on output response. Factor 'A' is used to represent the initial dye concentration and it is observed from the figure that dye decolorization increases with decrease in dye concentration. This is due that at higher dye concentration, the intermediate product formed blocks the active sites of the electrode and acts as resistance to current flow, which results in a decrease in the color removal. The effect of dye wastewater flow rate on decolorization is shown by a factor 'B'. Dye decolorization is increased with increase in wastewater flow rate. The increase in decolorization is due to the enhancement of the mass transfer coefficient at higher flow rate. The effect of current density on the color removal is denoted by 'C'. It is observed from the figure that dye decolorization increases with the increase in current density. This is due to the fact that more electrons are generated at higher current density, which results in an increase in the hypochlorite ion generation, which results in higher decolorization. The effect of supporting electrolyte concentration is denoted by 'D' on color removal. The current density increases the OCl^- generation, hence the dye decolorization increases. Various levels (1, 2, 3) of the operating parameter (A, B, C, D) and their mean color removal is shown in Table 3. It is observed from the table that Level '1' gives the highest color removal of 75.68% for the initial dye concentration. Level '4' shows the highest color removal of 58.15%, 69.96% and 62.29% for flow rate, current density and electrolyte concentration respectively.

Signal to noise (S/N) ratio

Using S/N ratio values in Taguchi analysis the optimal conditions of experimental parameters on color removal has been identified. In the Taguchi method, S represented 'signal' and N represented

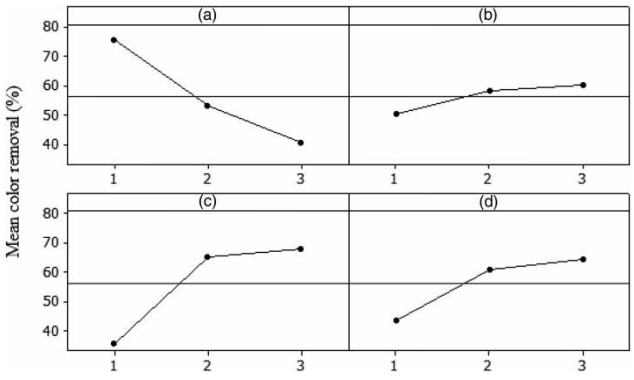

Figure 4 | Main effect plot for mean color removal of Acid red dye for different levels. (a) Dye concentration, (b) flow rate, (c) current density, (d) electrolyte concentration.

Table 3 | Mean color removal for electro-oxidation of Acid red 87 dye

Level	A	B	C	D
1	75.68	50.94	32.41	44.28
2	54.93	57.91	64.63	60.43
3	36.38	58.15	69.96	62.29

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'noise'. The S/N ratios are different for different types of experimental output response. In the present experiment, larger S/N ratio is better for higher decolorization. The values of the S/N ratios for the experimental parameters are shown in Table 4. The larger the S/N ratio, the higher the percentage color removal and vice versa (Yen & Li 2015; Pundir *et al.* 2018). It is observed from the table that the S/N ratio is level '1' for parameter 'A', and level '4' for parameters B, C and D respectively.

Table 4 | S/N ratio for electro-oxidation of Acid red 87 dye

Level	A	B	C	D
1	36.78	33.81	30.99	32.63
2	34.58	34.02	35.61	35.17
3	30.72	34.74	36.53	35.20

RTD modeling

Residence time distribution function E (t) is calculated for the pulse input of the tracer to the reactor using the Equation (2). The effect of different flow rates on E(t) is shown in Figure 5. This shows that increasing the flow rate, there is a decrease in residence time because less time is spent by the fluid inside the reactor. Based on the RTD information, mean residence time, variance and vessel dispersion number (D/UL) were calculated and the values are shown in Table 5. It is noticed that a lower dispersion number is observed for the flow rate 60 LPH. This is may be due to occurrence of back mixing which in turn reduces the dispersion number. It also noticed that (D/(UL) >0.1,

Table 5 | Residence time distribution parameters

Flow rate LPH	Mean residence sec	Variance sec^2	D/UL -
30	279.16	25,683.14	0.164
60	190.08	5,874.76	0.081
90	146.02	6,287.01	0.140

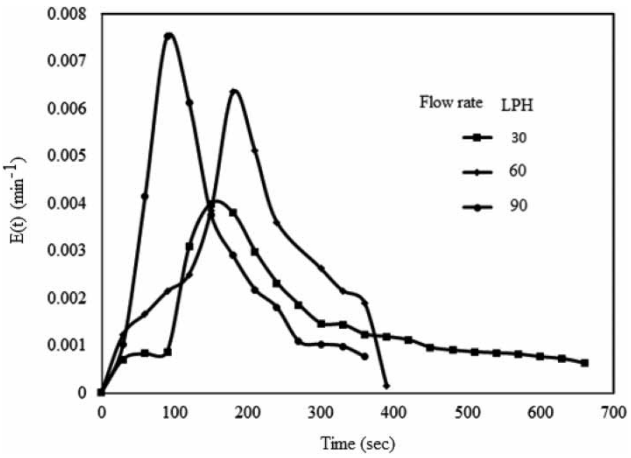

Figure 5 | Experimental E(t) distribution in a tubular electrochemical reactor for different flow rates.

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hence the reactor is modeled as an axial dispersion model and the model equation is (Mustoe & Wragg 1978; Susree *et al.* 2013):

$$C_A(t) = C_{A0} \exp\left\{\frac{-t}{\tau}\left(1 - \frac{4q.\exp[Pe/2]}{(1+q)^2 \exp[q.Pe/2] - (1-q)^2 \exp[-q.Pe/2]}\right)\right\} \quad (6)$$

where

$$q = \left[1 + \frac{4k\tau}{Pe}\right]^{0.5}, \; Pe = \frac{UL}{D}$$

D/UL is the dispersion number; k is the electrochemical reaction rate constant (min^{-1}); τ is the residence time (min); Pe is the Péclet number. The model value is compared with the experimental value and is shown in Figure 6. It is noticed from the figure that the model satisfactorily matches with the experimental result with a high correlation coefficient.

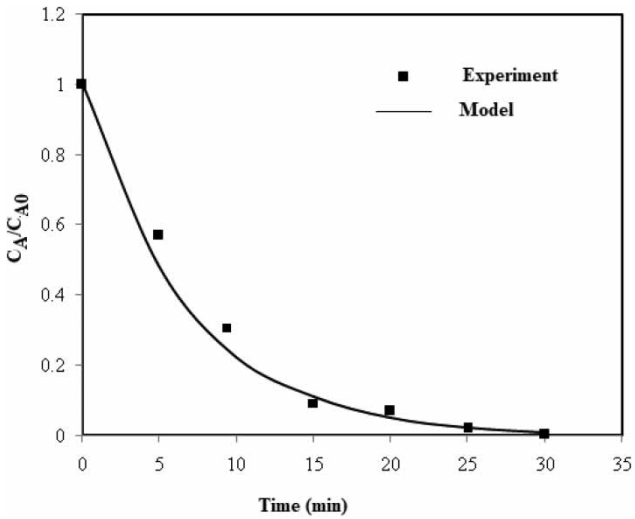

Figure 6 | Model comparison with experimental value. Flow rate 90LPH.

CONCLUSION

Decolorization of wastewater was performed in a tubular electrochemical reactor. Operating parameters such as dye concentration, flow rate, current density and supporting electrolyte concentration were studied for color removal and the parameters were optimized using Taguchi analysis. Kinetic modeling and RTD modeling for the tubular electrochemical reactor were performed. It is concluded from the experiment that color removal using an axial dispersion model satisfactorily matches the experimental color removal with a high correlation coefficient.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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