



Mathematical Modelling for Predicting Pollutant Removal Efficiencies of an Electrolysis System

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Abstract Electrolysis systems have been widely investigated for treating wastewater in laboratory-scale experiments, and most researchers reported efficient treatment outcomes. However, industrial scale implementation often necessitates assessing and prioritising various options involving different combinations of input parameters, which often requires mathematical models. This study presents mathematical models for predicting removal efficiencies of four different pollutants using electrolysis. Parametric equations were developed based on experimental results conducted in a previous study. Proposed equations are dependent on treatment

retention time and current intensity (voltage). Results revealed that the experimental data followed consistent patterns, which lead to the derivations of generalised equations which were able to closely predict pollutants' removal efficiencies obtained through experimental measurement. The developed equations also confirmed that beyond an optimum voltage, a further increase in voltage does not render higher removals of the pollutants, which is essential for enhancing the feasibility of industrial scale applications.

Keywords Electrolysis · Mathematical models · Removal efficiency · Pollutants · BOD · COD · TSS · TDS

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1 Introduction

Ever-increasing population and subsequent increase in consumptions cause generation of huge quantity of wastewater from different sources including domestic, commercial and industrial. Treatment and disposal of huge quantity of wastewater being generated are burdens for the urban authorities. Several technologies are available to treat the wastewater: chemical precipitation, filtration, microwave irradiation and air stripping. Some of these methods need expensive equipment, which makes the processes less feasible (Bonmatí and Flotats 2003). Another commonly used technique of wastewater treatment is electrolysis, which uses electrical energy to accelerate chemical separation, and if renewable energy sources are used for electrolysis, this method will

have very minimum environmental impacts (Zoulias et al. 2004). Electrolysis normally does not require neither expensive equipment nor any special chemicals. Moreover, this method produces very less sludge, which settles easily (Bayramoglu et al. 2006).

Electrolysis has been effectively used for treating various polluted water like poultry wastewater (Bayramoglu et al. 2006), laundry wastewater (Wang et al. 2009), industrial wastewater (Mahmoud and Hoadley 2012) and fly ash leachate (Tao et al. 2014). Kabuk et al. (2014) investigated removal of pollutants from leachate using electrocoagulation process. They have achieved removal efficiencies 60.5%, 92.4%, 60.8%, 28.3% and 28.9% for COD, total suspended solids (TSS), total organic carbon (TOC), total Kjeldahl nitrogen (TKN) and ammonia-nitrogen ($\text{NH}_3\text{-N}$) respectively. In another study, Fernandes et al. (2014) used a combined method of electrocoagulation process (ECP) with anodic oxidation (AO) in an effort to increase the biodegradability of landfill leachate. Through the ECP process, they have achieved a complete removal of chromium and a partial removal of zinc. Then, through subsequent AO process, the remaining zinc was removed. Also, they have reported an increase of iron during ECP, which was decreasing during subsequent AO process. Zailani et al. (2018) investigated pollutants removal efficiencies from leachate through electrocoagulation technique using aluminium electrode. They have reported that applying optimum conditions of current density (200 A/m^2), electrolysis duration (20 min) and pH value of 4.0 removals of COD, ammonia, colour, turbidity and suspended solids were 60%, 37%, 94%, 88% and 89% respectively. Ahsan et al. (2014) investigated a novel low-cost process, which uses activated carbon filtration along with electrolysis for treating leachate. They have achieved removal efficiencies of 75.6%, 57%, 72% and 83.1% for BOD, COD, TDS (total dissolved solids) and TSS (total suspended solids) respectively, with a retention time of 4 h and current of 7 V. However, when filtration with activated carbon was applied after electrolysis, removal efficiencies increased for all the pollutants mentioned above. With 4 h retention time, BOD removal efficiency increased from 54.6 to 61.5% at 3 V and from 66.4 to 70.5% at 5 V. Under the same conditions, COD removal efficiency increased from 7.5 to 38.5% at 3 V and from 31.1 to 49.5% at 5 V. Erabee et al. (2017) investigated the effect of NaCl, pH and electrode distance on the efficiency of electrolysis in treating turbidity, salinity,

TSS, TDS, BOD, COD and heavy metals (Zn and Mn). They have reported a most efficient condition: 60 V electric potential, 120 min retention time and 5% of NaCl solution using Al as anode and Fe as cathode (kept at a distance of 3 cm). Through optimum conditions, they have achieved a COD removal of 94% and Mn removal of 93%. Sousa et al. (2019) investigated effectiveness of electrolysis and photo-assisted electrolysis in the presence of chloride on removing pollutants (turbidity, conductivity, colour, pH, chlorides, TOC, COD and BOD) from dairy waste. They have achieved more than 90% removals of TOC and COD with only electrolysis (with chloride) and more than 95% removals of TOC and COD with photo-assisted electrolysis (with chloride).

All the above-mentioned studies on wastewater treatment efficiency using electrolysis and electrochemical methods are based on experiments only. For industrial implementation of such a process, it is often necessary to develop mathematical models of the investigated processes, which facilitates deciding design input parameters based on authorities' requirements and/or target removal criteria. Among the few mathematical modelling studies, Kabuk et al. (2014) used three-parameter optimization using the response surface method to propose optimum conditions of treating selected pollutants (i.e. COD, TSS, total organic carbon, TKN and ammonia-nitrogen $\text{NH}_3\text{-N}$). Eventually, they have proposed a second-order full polynomial model, which can replicate the results of their optimization studies. Curteanu et al. (2011) developed a simulation model using neural networks for predicting efficiency of removing algae (i.e. chlorophyll) from water through electrolysis. However, neural networks models are black box type model, which are not capable to readily provide output based on a particular input values. Gößling et al. (2018) developed a physically based numerical model to predict the behaviour of a proton exchange membrane electrolysis cell (PEMEC) depending on the current density, the operating conditions (cell temperature) and cell-specific parameters (electrical resistance of the cell, the membrane thickness and membrane conductivity). This method requires calibration to a specific electrolyser and its measured polarization curve. Such complex calibration is necessary due to the individual materials and production processes of the components.

It is not feasible to run experiments for each and every experimental condition or input parameter. Moreover, such experiments are always conducted in a small

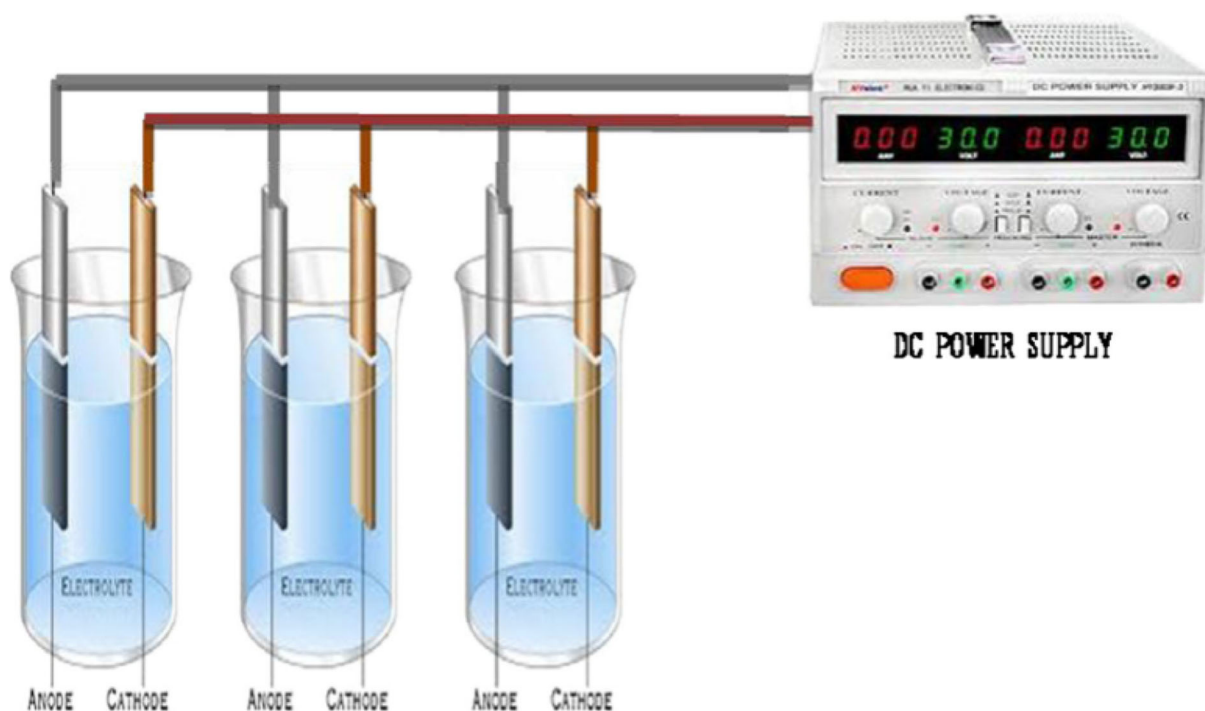


Fig. 1 Schematic diagram of experimental setup (source: Ahsan et al. 2014)

laboratory scale and performance of similar processes in a full industry scale setup requires translation of laboratory-scale data. Also, it is very expensive and time-consuming to conduct such laboratory- and industry-scale experiments to assess the removal efficiencies under numerous experimental conditions. In

Table 1 Removal efficiency measurements for different pollutants

Pollutant	Voltage (V)	Retention time (h)		
		1	2	4
BOD	3	12.7	36.9	58.7
	5	26.6	50.6	66.8
	7	36.4	60.1	75.6
COD	3	1.3	2.6	4.0
	5	3.0	10.8	18.5
	7	6.9	30.3	57.0
TSS	3	9.7	36.9	62.0
	5	51.0	63.3	77.6
	7	62.3	69.1	83.1
TDS	3	5.4	21.5	31.4
	5	31.9	54.0	66.3
	7	51.7	60.0	72.0

general, mathematical modelling study helps to reduce need of conducting numerous experiments and if successful can replicate different experimental conditions provided a good set of preliminary experimental data exists. Nonetheless, in many occasions, users do not prefer to use complex and/or black box type models, as those require specialised skills and software. Considering the above-mentioned issues, with the aim of developing a simple mathematical model, this paper presents development of generalised equations for the predictions of efficiencies of pollutants removals from wastewater based on an earlier conducted experimental study results. BOD, COD, TDS and TSS removal efficiency data collected in the study of Ahsan et al. (2014) were used for the parametric evolution of the model equations.

2 Data

Ahsan et al. (2014) conducted series of experiments on pollutants removal efficiencies for leachate samples collected from the Jeram Sanitary Landfill, Kuala Selangor, Malaysia, using a custom-made cylindrical glass reactor. In brief, the reactor was having 15 cm height, 4.5 cm

diameter and 240 mL capacity. A pair of electrodes made of iron having diameter of 3 mm and an effective surface area of 188 cm² were installed as the anode and cathode. The electricity was supplied to the electrodes via a digital direct current (DC) power supply (Model: Zhaoxin RXN 3010 DC 12 V 30 A). Figure 1 shows the schematic of an experimental setup.

The reactor was used to investigate the effects of different current densities (3, 5 and 7 V) and different retention times (1, 2 and 4 h) on pollutants removal efficiencies. The pollutants investigated were BOD, COD, TSS and TDS. Table 1 shows the measured removal efficiencies of these pollutants under different combinations and experimental conditions (i.e. current density and retention time).

3 Methodology

Measured data from the above-mentioned experiments were plotted with respect to retention time for all the three current densities. It is observed that for all the cases, the pollutant removal efficiencies follow a pattern

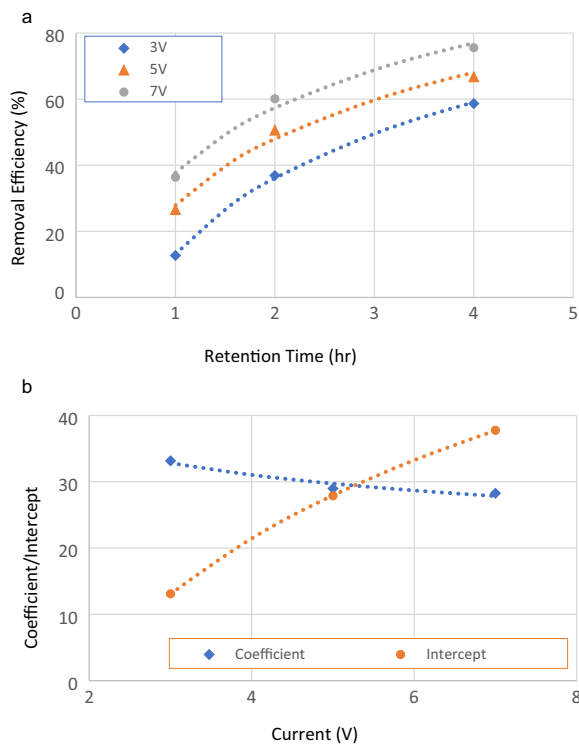


Fig. 2 **a** Relationship between BOD removal efficiency and retention time. **b** Relationship between BOD removal equation constants with voltage

with respect to the retention time; with the increase of retention time, removal efficiency also increases with a logarithmic pattern. This pattern can be replicated with the following equation:

$$RE = a \times \ln(RT) + b \quad (1)$$

where 'RE' is the removal efficiency, 'RT' is the retention time and 'a' and 'b' are the constants. For a particular pollutant, there will be three such equations, one for each current density (i.e. voltage). The equations can be written as follows:

$$RE_1 = a_1 \times \ln(RT) + b_1 \quad (2)$$

$$RE_2 = a_2 \times \ln(RT) + b_2 \quad (3)$$

$$RE_3 = a_3 \times \ln(RT) + b_3 \quad (4)$$

It is found that both the sets of 'a' (a_1, a_2, a_3) and 'b' (b_1, b_2, b_3) can be co-related with the voltage. The relationships follow as one of the following patterns:

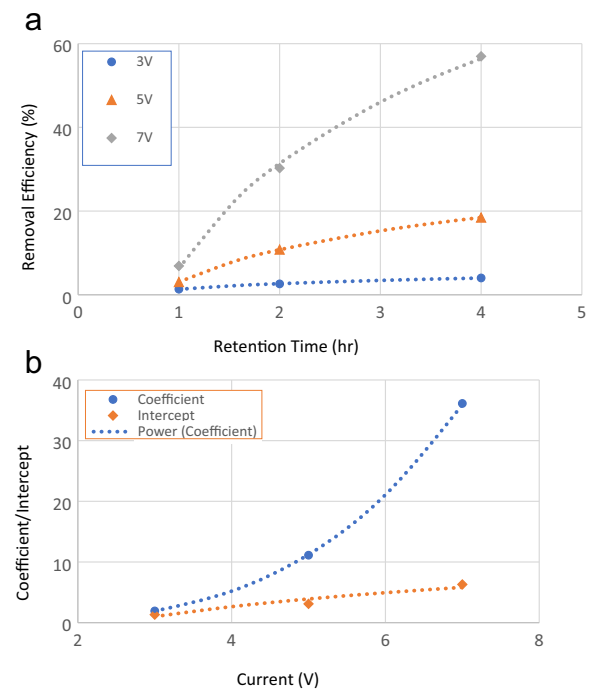


Fig. 3 **a** Relationship between COD removal efficiency and retention time. **b** Relationship between COD removal equation constants with voltage

$$a, b = c \times \ln(V) \pm d \quad (5)$$

$$a, b = c \times V^{\pm d} \quad (6)$$

where ‘ V ’ is the current density in voltage and ‘ c ’ and ‘ d ’ are the constants need to be derived.

Eventually, replacing equations for ‘ a ’ and ‘ b ’ in the Eq. 1, a generalised single equation is proposed for the removal efficiency of a particular pollutant. Similarly, all together, four such equations are developed, one for each of the BOD, COD, TSS and TDS. Eventually, results from the developed equations are compared with the real experimental measurements.

4 Results

Following sections describe derivations of generalised equation for each considered pollutant.

4.1 Removal Efficiency for BOD

Figure 2 a shows the graphs of BOD removal efficiencies with retention time for three different current densities. Logarithmic best-fit lines were drawn for all the three current densities (i.e. 3 V, 5 V and 7 V). The best-fit equations are as follows:

$$\text{For 3 V, } RT = 28.266 \times \ln(RT) + 37.768 \quad (7)$$

$$\text{For 5 V, } RT = 28.98 \times \ln(RT) + 27.889 \quad (8)$$

$$\text{For 7 V, } RT = 33.159 \times \ln(RT) + 13.096 \quad (9)$$

Coefficients (28.266, 28.98 and 33.159) and intercepts (37.768, 27.889 and 13.096) of these equations are drawn with voltage as an independent variable, and the plotted graphs are shown in Fig. 2b. From the best-fit lines of these graphs, it is found that the coefficients follow a power-function pattern with voltage, whereas the intercepts follow a logarithmic pattern with voltage. The best-fit equations are as follows:

$$a = 40.646 \times V^{-0.194} \quad (10)$$

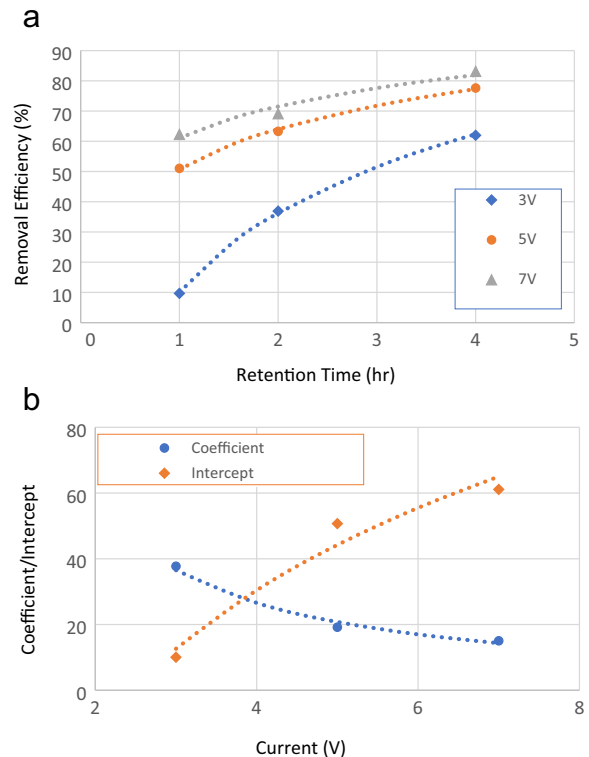


Fig. 4 a Relationship between TSS removal efficiency and retention time. b Relationship between TSS removal equation constants with voltage

$$b = 29.103 \times \ln(V) - 18.894 \quad (11)$$

where ‘ V ’ is the current density (i.e. voltage).

Substituting Eqs. 10 and 11 into Eq. 1, the final equation for the BOD removal efficiency is as follows:

$$RE = 40.646 \times V^{-0.194} \times \ln(RT) + 29.103 \times \ln(V) - 18.894 \quad (12)$$

4.2 Removal Efficiency for COD

Figure 3 a shows the graphs of COD removal efficiencies with retention time for three different current densities. Logarithmic best-fit lines were drawn for all the three current densities (i.e. 3 V, 5 V and 7 V). The best-fit equations are as follows:

$$\text{For 3 V, } RE = 36.128 \times \ln(RT) + 6.3327 \quad (13)$$

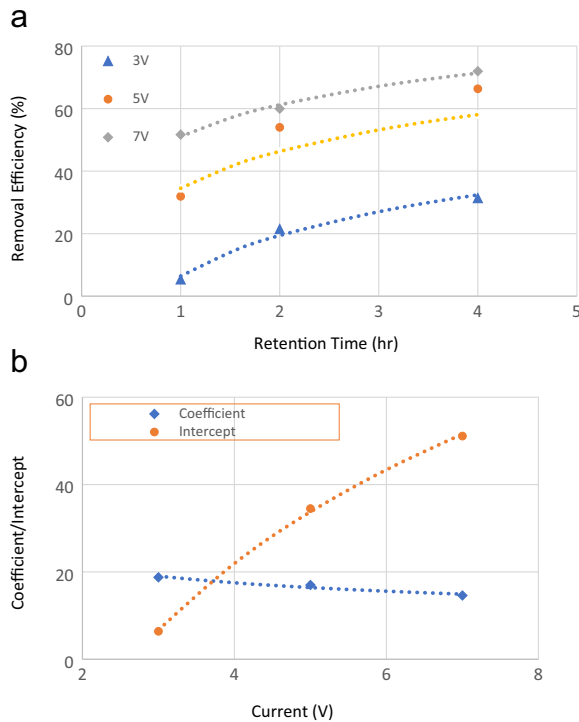


Fig. 5 **a** Relationship between TDS removal efficiency and retention time. **b** Relationship between TDS removal equation constants with voltage

$$\text{For 5 V, RE} = 11.115 \times \ln(\text{RT}) + 3.0619 \quad (14)$$

$$\text{For 7 V, RE} = 1.9299 \times \ln(\text{RT}) + 1.3172 \quad (15)$$

Coefficients (36.128, 11.12 and 1.93) and intercepts (6.34, 3.06 and 1.32) of these equations are drawn with voltage as an independent variable, and the plotted graphs are shown in Fig. 3b. From the best-fit lines of these graphs, it is found that the coefficients follow a power-function pattern with voltage, whereas the intercepts follow a logarithmic pattern with voltage. The best-fit equations are as follows:

$$a = 0.043 \times V^{3.4552} \quad (16)$$

$$b = 5.6823 \times \ln(V) - 5.2418 \quad (17)$$

Substituting Eqs. 16 and 17 into Eq. 1, the final equation for the COD removal efficiency is as follows:

$$\text{RE} = 0.0432 \times V^{3.4552} \times \ln(\text{RT}) + 5.6823 \times \ln(V) - 5.2418 \quad (18)$$

4.3 Removal Efficiency for TSS

Figure 4a shows the graphs of TSS removal efficiencies with retention time for three different current densities. Logarithmic best-fit lines were drawn for all the three current densities (i.e. 3 V, 5 V and 7 V). The best-fit equations are as follows:

$$\text{For 3 V, RE} = 15.044 \times \ln(\text{RT}) + 61.067 \quad (19)$$

$$\text{For 5 V, RE} = 19.175 \times \ln(\text{RT}) + 50.695 \quad (20)$$

$$\text{For 7 V, RE} = 37.725 \times \ln(\text{RT}) + 10.042 \quad (21)$$

Coefficients (15.04, 19.18 and 37.73) and intercepts (61.07, 50.7 and 10.04) of these equations are drawn with voltage as an independent variable, and the plotted graphs are shown in Fig. 4b. From the best-fit lines of these graphs, it is found that the coefficients follow a power-function pattern with voltage, whereas the intercepts follow a logarithmic pattern with voltage. The best-fit equations are as follows:

$$a = 123.04 \times V^{-1.105} \quad (22)$$

$$b = 61.839 \times \ln(V) - 55.319 \quad (23)$$

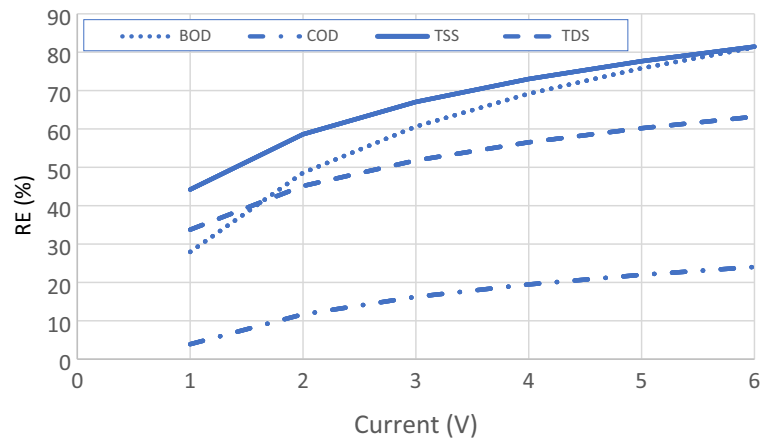
Substituting Eqs. 22 and 23 into Eq. 1, the final equation for the TSS removal efficiency is as follows:

$$\text{RE} = 123.04 \times V^{-1.105} \times \ln(\text{RT}) + 61.839 \times \ln(V) - 55.319 \quad (24)$$

4.4 Removal Efficiency for TDS

Figure 5a shows the graphs of TDS removal efficiencies with retention time for three different current densities. Logarithmic best-fit lines were drawn for all the three current densities (i.e. 3 V, 5 V and 7 V). The best-fit equations are as follows:

Fig. 6 Modelled removal efficiency patterns for different pollutants under varying retention times



$$\text{For } 3 \text{ V, RE} = 18.76 \times \ln(\text{RT}) + 6.393 \quad (25)$$

$$\text{For } 5 \text{ V, RE} = 17.0 \times \ln(\text{RT}) + 34.50 \quad (26)$$

$$\text{For } 7 \text{ V, RE} = 14.63 \times \ln(\text{RT}) + 51.062 \quad (27)$$

Coefficients (18.76, 17.0 and 14.63) and intercepts (6.393, 34.5 and 51.062) of these equations are drawn with voltage as an independent variable, and the plotted graphs are shown in Fig. 5b. From the best-fit lines of these graphs, it is found that the coefficients follow a power-function pattern with voltage, whereas the intercepts follow a logarithmic pattern with voltage. The best-fit equations are as follows:

$$a = 26.083 \times V^{-0.287} \quad (28)$$

$$b = 52.94 \times \ln(V) - 51.46 \quad (29)$$

Substituting Eqs. 28 and 29 into Eq. 1, the final equation for the TDS removal efficiency is as follows:

$$\text{RE} = 26.083 \times V^{-0.287} \times \ln(\text{RT}) + 52.94 \times \ln(V) - 51.46 \quad (30)$$

To assess the patterns of removal efficiencies for different pollutants, using the above-developed equations, removal efficiencies for all the four selected pollutants were calculated for a constant voltage (5 V) under varying retention times. Figure 6 shows the comparison of removal patterns for different pollutants

under varying retention times with a current of 5 V. From the figure, it is found that among these four pollutants, under same conditions, TSS removal efficiency is the highest showing a removal efficiency of 44% with 1 V and reaching up to an efficiency of 81% with 6 V. A similar removal efficiency can be achieved for BOD as well with 6 V current; however, for a lower voltage, BOD removal efficiencies are lower than the TSS removal efficiencies; with 1 V current, BOD removal efficiency is 28%. Lowest removal efficiencies are achieved for COD, an efficiency of 3.9% under 1 V and reaching up to 24% under 6 V. TDS removal efficiencies are in between, an efficiency of 34% under 1 V and reaching up to 63% under 6 V. From the figure, a general trend is observed that initially with a low current, the rate of increase of removal efficiency increases with a higher rate; however, with the higher current, the rate of increase of removal efficiency reduces and at one stage becomes 0, i.e. beyond a certain value, removal efficiency does not increase anymore with the increase of voltage. As such, an optimum level of voltage exists, beyond which increase in voltage will not render higher removal efficiency.

5 Comparison and Conclusion

The accuracy of developed equations was assessed through calculating removal efficiencies using the relevant developed equation for a particular pollutant for different input values of retention times and current densities, for which measured values are available. For the current study, measured removal efficiencies were available for nine combinations of retention times and

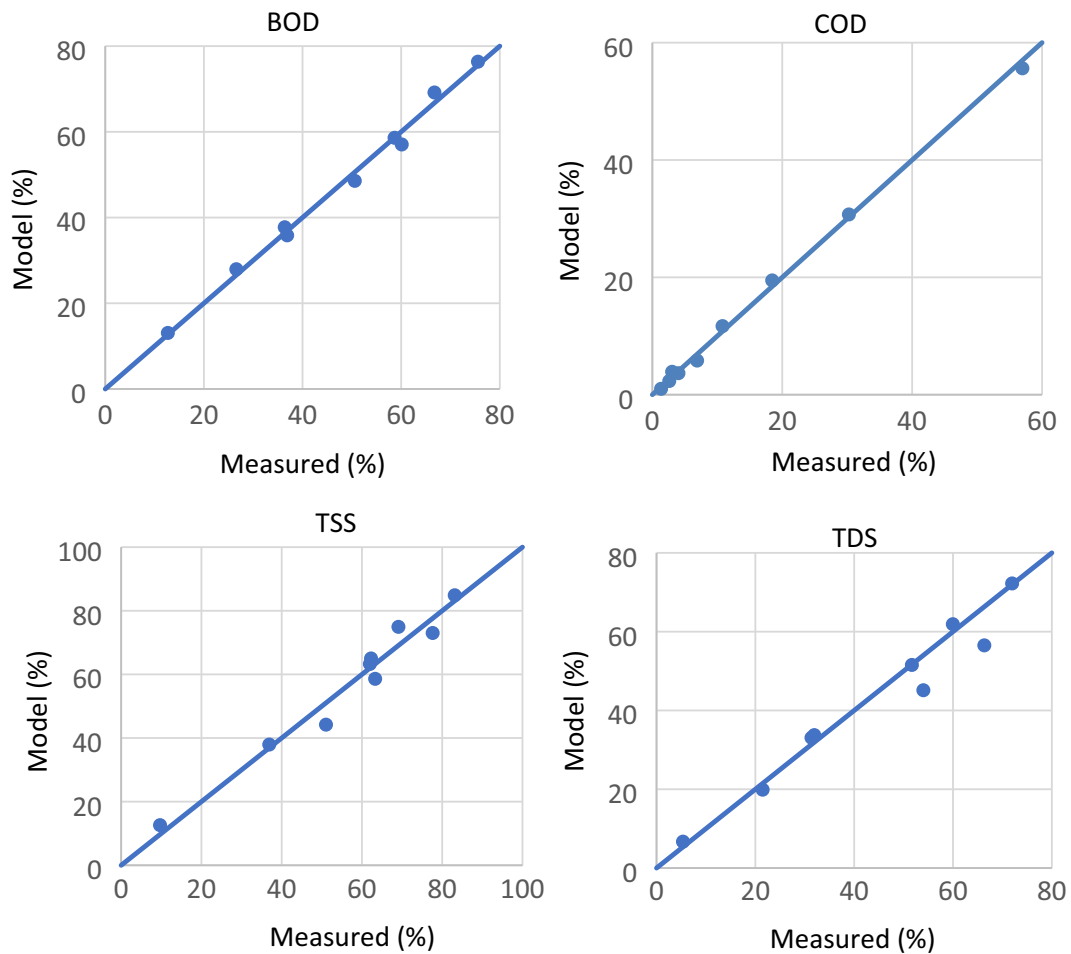


Fig. 7 Comparisons of model calculated values with the measured values of removal efficiency

current densities. As such, for each pollutant, there are nine calculated values; each calculated value corresponds to a measured value of removal efficiency. Calculated values of removal efficiencies were plotted with the corresponding measured values for all the pollutants. Figure 7 show the comparisons of model calculated values with the measured values for all the four pollutants considered in this study. In each figure, a line was

drawn with an angle of 45° to show the ideal position of the scattered points. From the figures, it is clear that the developed equations are able to predict pollutant removal efficiencies for all the selected pollutants with good accuracy. For BOD, COD, and TSS, the simulations are very close to the experimental measured values. For TDS, the simulations are also good, except for two measurements, where measured values were bit higher than the calculated removal efficiencies. Apart from these two values, all other values are closely matching with the measured values. As such, it can be concluded that the developed equations are quite successful in predicting removal efficiencies based on retention time and current density (i.e. voltage). Table 2 shows the root mean squared error (RMSE) values of the simulations for all the four pollutants. It is to be noted here that in the original experimental study, there were only three measurements for each combination of retention time and

Table 2 Root mean squared error (RMSE) values of the simulations

Parameters	RMSE
BOD	1.67
COD	0.82
TSS	4.03
TDS	4.59

voltage. Due to limited data availability, the equations were developed only with three data, which one may question towards the validity of such model. However, as the developed models are not statistical models, three data points are still acceptable. Nonetheless, one may question the validity of developed equations beyond the ranges of considered independent variables (i.e. retention time and voltage). As such, it is recommended that future similar experimental study should consider wider ranges of these variables.

Such modelling exercise is useful for the stakeholders, who want to implement similar industrial scale pollutants treating facility. This sort of equations will help in decision-making on selecting input parameters (i.e. for this case retention time and current density) to achieve certain target removal efficiency. It is to be noted that developed equations are valid for the particular type of electrodes used in this study having same ratio of electrode surface area to the wastewater volume. A future study is recommended to explore effect of ratio of electrode surface area to the wastewater volume. Nonetheless, for any type of electrodes with different combinations of device parameters, similar methodology can be applied to develop similar removal efficiency equations. Such methodology has never been applied for the study of pollutant removal efficiency using electrolysis.

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