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Developing mathematical relations between concentrations, electrical conductivity and temperature of methylene blue, methyl violet 2B and NaCl in water

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ABSTRACT

Methylene blue (MB), Methyl violet 2B (MV2B) and NaCl are known as three common industrial contaminants. This paper seeks to use electrical conductivity (EC) and temperature (*T*) values to evaluate the concentration (*C*) of these components, rather than using sophisticated equipment/procedure that may increase the likelihood of machine/human errors. EC and *T* are measurable parameters with cheap instruments, and they also could be monitored in real time. Concentrations between 0 to 1,100 mg/L are used in order to model the correlation between *C*, EC and *T*. Three mathematical models are presented in this paper for each contaminant. The first model is derived from the average ratio of EC/*C*, and the influence of temperature on EC in constant *C* is not taken into account. The results of this study illustrate that accuracy rate (*R*) would be 0.88, 0.86, 0.88 for MB, MV2B, NaCl, respectively. The second and third models indicate the best polynomial relation between *C*, EC and *T*. These models investigate the effects of temperature variation between 15°C and 35°C on the correlation between *C* and EC. *R* values will be increased for MB, MV2B and NaCl. The current study found that in the polynomial relation, EC power more than 2 and *T* power more than 1 does not significantly increase the accuracy of models. The models can be employed so as to estimate the concentration of these three compounds in experimental/practical purposes. This method can be developed for experimental/practical applications that deal with concentration and TDS measurement. Another important finding is that the temperature has a direct effect on the measurements of EC meter, which may lead to errors that can be mitigated by the described method. This study takes the effect of temperature on the EC readings into consideration while the previous similar researches just modeled the relationship between EC and TDS by averaging the ratio between the TDS and EC values without considering temperature effects.

Keywords: Electrical conductivity; Temperature; Methylene blue; Methyl violet 2B; NaCl; Mathematical modeling

1. Introduction

Water resources are encountered with different issues including industrial and synthetic pollutions. These issues are expected to rise in the upcoming decades [1,2]. Synthetic dyes are the main pollutants in water sources and wastewater because dye contamination in wastewater can appear in various types. For example, the presence of dyes in water, even in very low quantities, is highly visible and

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undesirable. In addition, color interferes with penetration of sunlight into waters, retards photosynthesis, inhibits the growth of aquatic biota and interferes with gas solubility in water bodies [3–6].

Among dyes, Methylene blue (MB) and Methyl violet 2B (MV2B) are two common ones and a large number of researchers have focused their attention on removing them from water resources. For instance, Sarici-Ozdemir and Bello et al. studied kinetics of adsorption and desorption of MB on activated carbon that is one of the most effective and common dyes adsorbents [7,8]. However, this method is expensive and costly to adopt [9]. Other studies conducted by Almeida et al. [3], Feddal et al. [10] and Baybars et al. [11] illustrated removing MB from dye-containing effluents by absorption on montmorillonite clay. In addition, Duan et al. [6] obtained the optimal conditions for MB removal by electrocoagulation with response surface method.

Augustine et al. [4] investigated the effects of temperature and pH on equilibrium bio sorption of MV2B and Awin et al. [12] worked on removing MV2B by using $BaSr_2NbO_{5.5}$. Saeed et al. [13] studied on photo degradation of MV2B with photocatalyst [13]. Dahri et al. [14] removed MV2B by adsorption on Jackfruit seeds.

Another interesting category that captured the attention of many researchers in recent years has been impacts, removing and measurement of salts in water resources. For example, some researchers such as Shrestha et al. [15], Farag and Harper [16], and Grasso et al. [17] studied the impacts of salts, including NaCl, on the aquatic environment, while others, such as Endarko et al. [18] and Wajima et al. [19] worked on removing them from aquatic bodies.

A new simple method, which has been widely used in the recent years is based on electrical conductivity (EC). EC could be measured easily with cheap and simple equipment [20,21]. EC is measured by an electronic probe, which applies a voltage between two electrodes. The electrical resistance of water is measured by the drop in the voltage [22]. Many researchers believe that total dissolved solids (TDS) of water has a direct correlation with EC [22–28]. Eq. (1) shows a proper estimation to calculate the value of TDS [22–25,29].

$$\text{TDS} = \alpha \times \text{EC}\ (\mu\text{S/cm}) \tag{1}$$

TDS meters estimate TDS value based on this equation but α is not a constant value. Thirumalini and Joseph [25], Rusydi [26], Ayers and Westcot [27] estimated that the best value for α is 0.5–0.75, 0.55–0.7, and 0.64, respectively. Salami and Ehteshami [20] calculated α value equal to 0.5 as the best approximation for estimation of salinity value of San Joaquin River basin (California, USA). Given the impacts of temperature on ions movement in solution, we may have a variety of EC readings in constant TDS (s) in different temperatures [30].

Salami Shahid and Ehteshami [20], Salami Shahid and Ehteshami [23] Salami et al. [31], and Salari et al. [32] used EC, temperature (T) and pH to estimate quality parameters of several rivers by mathematical equations or neural network modeling.

The aim of this paper is to determine accurate model(s) to obtain the concentration of MB, MV2B and NaCl considering EC and T values. These three different compounds are chosen to examine whether the method is applicable for various compounds.

This paper has been organized in the following ways:

- Deploying simple mathematical modeling for estimating the concentrations of desired compounds,
- Considering EC and T measurements in the modeling, and
- Estimating the concentrations of mentioned compounds by the proposed model, instead of using complicated equipment and procedures.

The proposed procedure for modeling could be implemented in similar projects and will be highly beneficial for experimental and practical purposes. This paper deeply delves into the procedure in different experiments.

2. Methods and materials

2.1. Samples preparation

The required amount of desired compound is weighted by a laboratory scale with accuracy range of 0.1 mg. Then, the weighted compound is added to 1,000 mL of distilled water with EC ≤ 5 μS/cm and following that is mixed with a magnetic stirrer mixer for 2 min.

Eutech Cyber CON 110 EC meter is used for measuring EC and T. In addition, DR 5000 Spectrophotometer is used to obtain the C values (see the Hatch company manual for DR 5000) [33].

2.2. Measurements

Over 200 measurements were obtained for each compound, but only 175 measurements were utilized for modeling. Others were eliminated from the study as the error of measurement process since they were beyond the modeling range or had obvious errors, such as very high or low EC readings.

Varied concentration of a compound was added to distilled water. In the next stage, various temperatures from 13°C to 38°C were applied and EC was recorded in each temperature. The value of EC of distilled water is deduced from EC readings. A preliminary diagram of EC-T was drawn for each concentration. Following that, the readings that were inconsistent with the approximate trend were eliminated as the measurement errors. As stated, in constant concentration, EC value rises with rising temperature [34,35]. For example, in constant concentration, if EC reading in 28°C (EC_{28}) is higher than EC_{32} and the EC_{32} value is consistent with the approximate trend of the diagram, then the EC_{28} reading is eliminated as the error of measurement.

Range of concentration was varied from 0 to 1,100 mg/L for each compound.

2.3. Modeling

Three models are developed for each compound:

The first model is based on the average value of C/EC. Previous similar studies made attempts to assess TDS value by this method without regard to the effect of temperature on EC value.

$$C = \alpha.\mathrm{EC} \tag{2}$$

$$\alpha = \frac{1}{175} \times \sum_{1}^{175} \frac{C_i}{\mathrm{EC}_i} \tag{3}$$

where C_i is the concentration of compound in test number i and EC_i is the electrical conductivity in test number i.

This investigation makes an effort to determine more accurate, reliable and practical models that address the effect of temperature on EC value, considering the regression method instead of simple averaging that was used in previous studies [22–28].

The second one is conducted given the changes of the relation made between EC and concentration in various temperature. It is obvious that as EC rises, the temperature increases [34,35], while the concentration is constant and remains unchanged because ions are not fixed and constantly moving in the higher temperatures. Following equations highlight the relationship:

$$\frac{\mathrm{EC}}{C} = \alpha_1.T + \alpha_2 \tag{4}$$

Or

$$C = \frac{\mathrm{EC}}{\alpha_1.T + \alpha_2} \tag{5}$$

where α_1 and α_2 are constant that could be calculated by interpolation methods.

The third model for each compound is developed given that the relation between EC and concentration changes with variation of EC (in constant temperatures), as follows:

$$\frac{\mathrm{EC}}{C} = \sum_{i=0}^{n} \sum_{j=0}^{n} \alpha_{i,j}.T^{i}.\mathrm{EC}^{j} \tag{6}$$

This equation represents an n degree polynomial with two variables (T, EC), in which $\alpha_{i,j}$ (s) are the coefficients of equation that could be estimated by interpolation methods.

In this paper, R^2 and accuracy rate (R) values are selected so that the accuracy of models is displayed, as follows:

$$R^2 = 1 - \frac{\mathrm{SS}_{\mathrm{res}}}{\mathrm{SS}_{\mathrm{tot}}} \tag{7}$$

where

$$\mathrm{SS}_{\mathrm{tot}} = \sum_i (y_i - \bar{y})^2 \tag{8}$$

$$\mathrm{SS}_{\mathrm{res}} = \sum_i (y_i - f_i)^2 = \sum_i \mathrm{error}_i^2 \tag{9}$$

$$R = \frac{1}{175} \sum_i \left(1 - \frac{|y_i - f_i|}{y_i} \right) \tag{10}$$

where y_i is real data, number i, f_i is the ith estimation result, and $\bar{y}$ is the average of real data.

Calculations for estimating the coefficients of models are made in MATLAB software. MATLAB has a toolbox named curve/surface fitting tool. This toolbox assists users in inputting the data series into software and choosing the method of modeling. These methods comprise interpolation, polynomial fitting and custom equation. The software employs mathematical procedures such as regression to minimize the squared error, which also maximizes the R^2 value.

In this study, all of these methods undergo tests, and the best results are achieved by polynomial fitting. In polynomial fitting tool, one can define the highest degree for each variable, and the software will calculate the optimum combination of the coefficient of equation/polynomial to find the best model with the least error.

3. Results

It seems that for concentration lower than 20 mg/L, concentration is less likely to have a constant relationship with EC. In constant concentration lower than 20 mg/L, we could change EC(s) with regard to micro streams around EC meter probe. In addition, the concentration and EC are not constant in different places of container, top to bottom and edges to center of the container. Accordingly, resulted measures for concentration below 20 mg/L were removed.

Data series for MB, MV2B and NaCl according to the presented procedures are introduced in this section. The produced data are shown in Figs. 1–3. After data production, they are used in MATLAB curve/surface fitting section to estimate the best combination of coefficients of equations that leads to the highest R^2 (s).

From the data in Fig. 1, standard deviation for T, EC and C are 5.54°C, 95.31 µS/cm and 333.10 mg/L, respectively. Mean value of these three parameters is 26.19°C, 104.27 µS/cm and 369.95 mg/L. The minimum and maximum value of these parameters are 16°C and 37.8°C, 6.05 and 360.4 µS/cm, 28 and 1,040 mg/L.

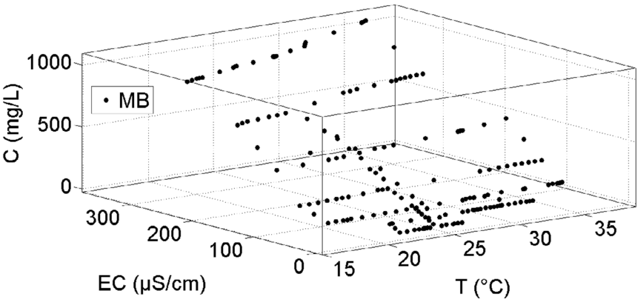

Fig. 1. Raw data produced for modeling MB.

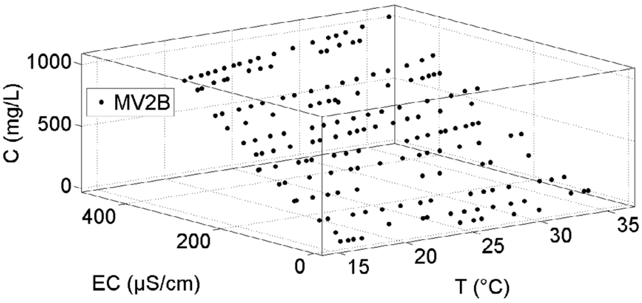

Fig. 2. Raw data produced for modeling MV2B.

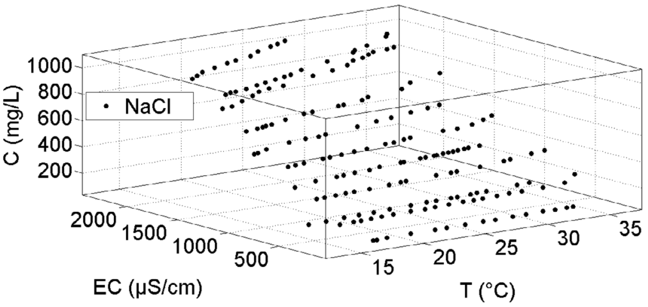

Fig. 3. Raw data produced for modeling NaCl.

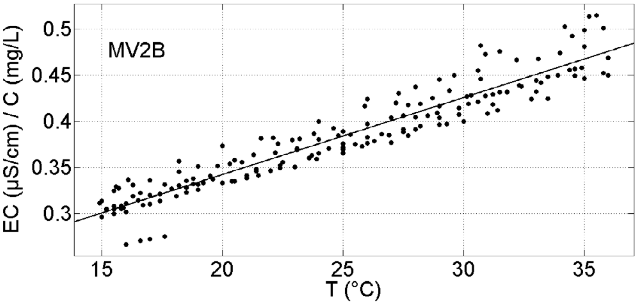

Fig. 5. Relation between EC/*C* and *T* for MV2B.

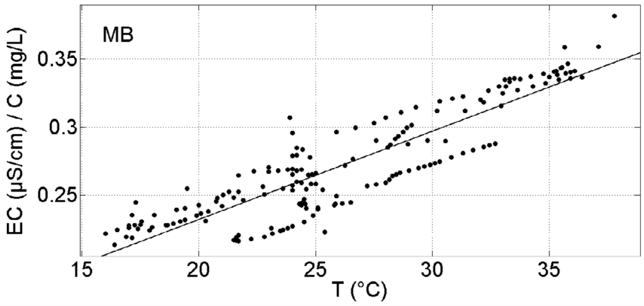

Fig. 4. Relation between EC/*C* and *T* for MB.

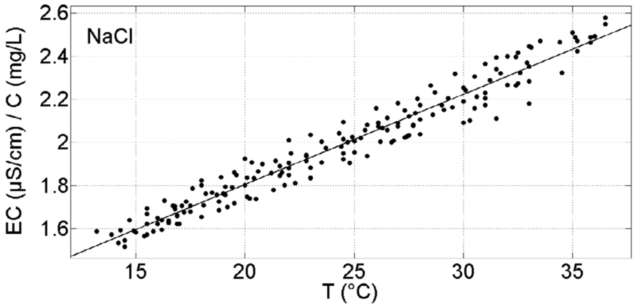

Fig. 6. Relation between EC/*C* and *T* for NaCl.

As shown in Fig. 2 standard deviations for *T*, EC and *C* are 6.27°C, 118.55 μS/cm and 316.00 mg/L, respectively. Mean values of these three parameters are 24.80°C, 208.24 μS/cm and 544.70 mg/L. The minimum and maximum values of these parameters are 14.9°C and 36°C, 9.4 and 471 μS/cm, 24 and 1,035 mg/L.

Fig. 3 shows that standard deviation for *T*, EC and *C* are 6.22°C, 593.65 μS/cm and 300.98 mg/L, respectively. Mean values of these three parameters are 24.23°C, 1,018.63 μS/cm and 519.81 mg/L. The minimum and maximum values of these parameters are 13.2°C and 36.5°C, 146.8 and 2,330 μS/cm, 85 and 1,053 mg/L.

Figs. 1–3 indicate that the relation of EC and *C* is almost linear. The reason for this is the electrical conductivity due to ions movement in solution; so, more dissolved material leads to more ions movement. In constant *C*, rising temperature causes more ions movement, resulting in EC value increment. The relationship between EC and temperature in constant *C* is also a linear relationship.

Figs. 4–6 confirm that the relation between EC/*C* and *T* in constant concentrations is linear.

As presented in Fig. 4, the standard deviation of the EC/*C* values is 0.040 μS mg/cm L, their average is 0.272 μS mg/cm L and the minimum and maximum them are 0.213 and 0.381 μS mg/cm L.

As indicated in Fig. 5, the standard deviation of the EC/*C* values is 0.055 μS mg/cm L, their average is 0.382 μS mg/cm L and the minimum and maximum them are 0.267 and 0.515 μS mg/cm L.

Fig. 6 shows that the standard deviation of the EC/*C* values is 0.267 μS mg/cm L, their average is 1.982 μS mg/cm L and the minimum and maximum of them are 1.517 and 2.579 μS mg/cm L.

Table 1
Statistical data of the produced data

		EC (μS/cm)	EC/*C* (μS mg/cm L)	*C* (mg/L)	*T* (°C)
MB	SD	95.31	0.040	333.10	5.54
	Average	104.27	0.272	369.95	26.19
	Minimum	6.1	0.213	28	16.0
	Maximum	360.4	0.382	1,040	37.8
		EC	EC/*C*	*C*	*T*
MV2B	SD	118.55	0.055	316.00	6.27
	Average	208.24	0.382	544.70	24.80
	Minimum	9.4	0.267	24	14.9
	Maximum	471.0	0.515	1,035	36.0
		EC	EC/*C*	*C*	*T*
NaCl	SD	593.65	0.267	300.98	6.22
	Average	1,018.63	1.982	519.81	24.23
	Minimum	146.8	1.517	85	13.2
	Maximum	2,330.0	2.579	1,053	36.5

SD stands for standard deviation.

Statistical data of the produced data come in Table 1:

In the modeling procedure, according to R^2 value, it was deduced that the best combination for the third case of models for all three compounds is the second-degree polynomial with degree 2 for EC and degree 1 for *T*. Thus, the general form of third models would be as follows:

$$\frac{\mathrm{EC}}{C} = \alpha_0+\alpha_{1,0}.T+\alpha_{0,1}.\mathrm{EC}+\alpha_{1,1}.T.\mathrm{EC}+\alpha_{0,2}.\mathrm{EC}^2 \tag{11}$$

Or

$$C = \frac{\mathrm{EC}}{\alpha_0 + \alpha_{1,0}.T + \alpha_{0,1}.\mathrm{EC} + \alpha_{1,1}.T.\mathrm{EC} + \alpha_{0,2}.\mathrm{EC}^2} \quad (12)$$

The best precision of models is achieved when the power degrees of EC and T are 2 and 1, respectively, in models. Results showed that increasing the power degree of EC and T does not significantly increase the accuracy of models. Different power degrees for EC and T are tested and R^2 values for all of them are presented in Table 2. As the results show, for higher degrees than the polynomial equation presented in Eq. 11, R^2 value does not increase significantly and even reduces in some cases.

Table 2
Results of testing the effect of different power degrees for EC and T on R^2 values

R^2 values for different power degrees for EC					
Power degree for EC	1	2	3	4	5
MB	0.9871	0.9979	0.9981	0.9979	0.9965
MV2B	0.9824	0.9941	0.9943	0.9938	0.9932
NaCl	0.9867	0.9982	0.9985	0.9983	0.9980
R^2 values for different power degrees for EC					
Power degree for T	1	2	3	4	5
MB	0.9979	0.9983	0.9981	0.9975	0.9963
MV2B	0.9941	0.9942	0.9938	0.9932	0.9924
NaCl	0.9982	0.9984	0.9981	0.9970	0.9954

Table 3 illustrates the models and Figs. 7–9 show the comparison between the results developed by the mathematical models and real data.

It is apparent from Figs. 7–9 that the first models that do not consider temperature have more errors than the second and third models. The third model has the best consistency with the real data. These figures also imply that estimating concentration/TDS just with respect to EC value is not proper. In higher temperatures, the EC is higher. These results prove that the procedure of concentration/TDS calculation should consider the effect of temperature on EC.

Additional 12 tests with four values of concentrations between 74 and 1,053 mg/L in three different temperatures between 15°C and 36°C are conducted for each compound. In these tests, tap water with EC value of 745 μS is used instead of distilled water. Results of these tests show that if 745 μS is subtracted from overall EC of solution (Eq. (13)), models can calculate the C value with the similar accuracy rates as before. The results of these 36 tests are shown in Table 4.

$$\mathrm{EC}' = \mathrm{EC} - \mathrm{EC}_w \quad (13)$$

where EC is the total EC of the solution made by tap water. EC_w is the EC of tap water that in our tests was equal to 745 μS/cm. If tap water is used instead of distilled (EC = 0) water, EC′ is considered in models instead of EC value for estimation of intended compound.

In terms of comparison, other three different types of EC meters are employed for measurement. The results showed that the models could estimate the concentrations by using

Table 3
Resulted mathematical models for each compound

Methylene Blue		
First model	$C_{\mathrm{MB}} = 3.75 \times \mathrm{EC}$	Eq. (13) $R^2 = 0.939$ $R = 0.88$
Second model	$C_{\mathrm{MB}} = \dfrac{10{,}000 \times \mathrm{EC}}{65.05 \times T + 1{,}018}$	Eq. (14) $R^2 = 0.993$ $R = 0.94$
Third model	$C_{\mathrm{MB}} = \dfrac{10{,}000 \times \mathrm{EC}}{942.5 + 57.42 \times T + 3.545 \times \mathrm{EC} + 0.0672 \times \mathrm{EC} \times T - 0.01413 \times \mathrm{EC}^2}$	Eq. (15) $R^2 = 0.998$ $R = 0.97$
Methyl Violet 2B		
First model	$C_{\mathrm{MVB2}} = 2.67 \times \mathrm{EC}$	Eq. (16) $R^2 = 0.931$ $R = 0.86$
Second model	$C_{\mathrm{MVB2}} = \dfrac{10{,}000 \times \mathrm{EC}}{77.06 \times T + 1{,}903}$	Eq. (17) $R^2 = 0.993$ $R = 0.94$
Third model	$C_{\mathrm{MVB2}} = \dfrac{10{,}000 \times \mathrm{EC}}{1{,}205 + 109.5 \times T + 3.016 \times \mathrm{EC} - 0.1287 \times \mathrm{EC} \times T - 0.000855 \times \mathrm{EC}^2}$	Eq. (18) $R^2 = 0.994$ $R = 0.95$
NaCl		
First model	$C_{\mathrm{NaCl}} = 0.51 \times \mathrm{EC}$	Eq. (19) $R^2 = 0.921$ $R = 0.88$
Second model	$C_{\mathrm{NaCl}} = \dfrac{10{,}000 \times \mathrm{EC}}{418 \times T + 9{,}691}$	Eq. (20) $R^2 = 0.997$ $R = 0.97$
Third model	$C_{\mathrm{NaCl}} = \dfrac{10{,}000 \times \mathrm{EC}}{10{,}370 + 436.1 \times T + 1.657 \times \mathrm{EC} - 0.02378 \times \mathrm{EC} \times T + 0.0008295 \times \mathrm{EC}^2}$	Eq. (21) $R^2 = 0.998$ $R = 0.98$

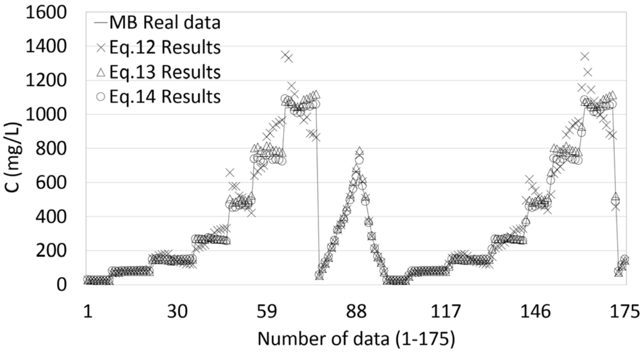

Fig. 7. Comparing between real data and mathematical models for MB.

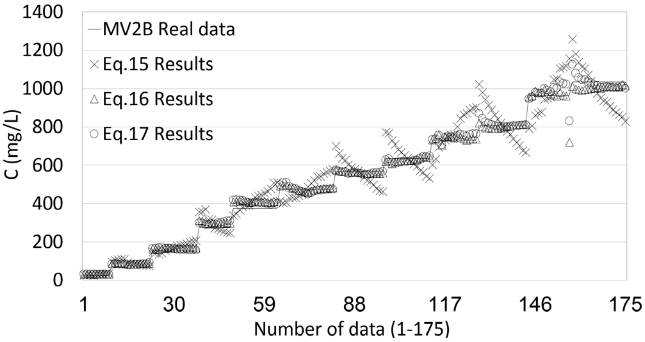

Fig. 8. Comparing between real data and mathematical models for MV2B.

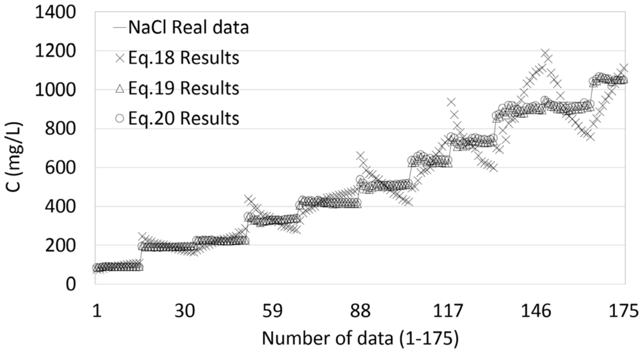

Fig. 9. Comparing between real data and mathematical models for NaCl.

any type of EC meter. The difference in results is negligible and comes from the different calibration of each EC meter device.

4. Conclusions

This study reveals that simple mathematical models can be applied for deriving accurate and reliable models for evaluation of the concentrations of different solved contaminants. These models are developed based on EC and *T* values as two measurable parameters. This method could reduce the cost and errors of measurement, and provide the capability of real-time monitoring.

Table 4
Results of models with using tap water instead of distilled water

C (mg/L)	*T* (°C)	EC (μS/cm)	EC′ (μS/cm)	*C* (mg/L)	*C* (mg/L)	*C* (mg/L)
			Methylene Blue			
				Eq. (13)	Eq. (14)	Eq. (15)
83	24.5	764.1	19.1	71.63	73.13	78.17
83	29.4	767.4	22.4	84.00	76.44	81.54
83	32.7	768.9	23.9	89.63	75.99	81.04
460	17.3	857.4	112.4	421.50	524.41	491.59
460	25.9	881.3	136.3	511.13	504.29	472.02
460	33.5	899.4	154.4	579.00	482.93	450.91
754	17	915.2	170.2	638.25	801.37	737.72
754	29.3	982.4	237.4	890.25	811.91	756.64
754	35.3	1,002.4	257.4	965.25	776.64	723.78
1,040	16	975.4	230.4	864.00	1,119.10	1,059.00
1,040	24.7	1,020.4	275.4	1,032.75	1,049.25	1,011.57
1,040	35.8	1,105.4	360.4	1,351.50	1,076.85	1,089.65
			R^2=	0.886	0.989	0.997
			Methyl Violet 2B			
				Eq. (16)	Eq. (17)	Eq. (18)
74	16.3	768.5	23.5	62.75	74.39	78.05
74	25	772.8	27.8	74.23	72.59	70.63
74	35.5	782.1	37.1	99.06	79.98	73.71
275	15.5	833.3	88.3	235.76	285.08	295.74
275	20.5	842.5	97.5	260.33	279.95	280.30
275	30.9	874	129	344.43	301.11	289.86
636	15.5	940	195	520.65	629.55	635.41
636	26.3	985	240	640.80	610.74	608.04
636	35	1,028	283	755.61	615.20	622.28
1,035	15	1,051	306	817.02	1,000.36	987.22
1,035	22.4	1,106	361	963.87	994.72	1,004.33
1,035	35.8	1,212	467	1,246.89	1,001.77	1,113.12
			R^2=	0.918	0.996	0.993
			NaCl			
				Eq. (19)	Eq. (20)	Eq. (21)
85	16.8	887.8	142.8	72.83	85.44	79.96
85	26	927.5	182.5	93.08	88.77	83.45
85	33.5	954	209	106.59	88.21	83.19
216	16.3	1,118	373	190.23	226.00	209.12
216	24.3	1,185	440	224.40	221.68	206.75
216	32.5	1,266	521	265.71	223.84	210.26
615	15.5	1,786	1,041	530.91	643.78	592.42
615	26.5	2,044	1,299	662.49	625.48	594.21
615	32.9	2,201	1,456	742.56	621.08	600.84
1,053	15	2,411	1,666	849.66	1,043.79	993.12
1,053	25.3	2,871	2,126	1,084.26	1,049.03	1,068.46
1,053	35.4	3,291	2,546	1,298.46	1,039.68	1,131.23
			R^2=	0.923	0.999	0.993

Results show that measuring EC cannot solely evaluate the concentration of a specific compound. Thus, temperature was considered in the modeling, due to its effects on

EC value. Three models are developed here. The first one does not consider the temperature, but the second and third ones account for the temperature as an effective parameter. The second and third models have higher precision in the estimation of concentration.

This study showed that the temperature has direct effects on the measurements of EC meter, which may lead to errors. This error can be mitigated by applying the described method. This study considered the effect of temperature on the EC readings while similar previous researches just modeled the relationship between EC and TDS by averaging the ratio between the TDS and EC value without considering the temperature effect.

The results of this study also showed that the EC/C ratio is not a constant value in different temperatures. However, previous studies usually estimated TDS value by multiplying a constant coefficient and EC value, which cannot be acceptable in different environmental conditions.

In practical applications, the presented models can be employed to estimate the amount of a contaminant, which should be added to a solution to achieve a specified EC. The models can also be used to estimate the concentration of a contaminant, when the concentration measurement equipment is not available.

Finally, the studies showed that if, as a solvent, tap water is used instead of distilled water, models will be also applicable for evaluating the concentration of compounds.

Models similar to those represented here could be simply derived and deployed for checking the operators' and/or equipment's errors in the experimental and practical applications related to the concentration measurements.

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