Chemical Engineering Journal 147 (2009) 161–172

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Prediction of cell voltage and current efficiency in a lab scale chlor-alkali membrane cell based on support vector machines

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ARTICLE INFO

Article history:
Received 14 November 2007
Received in revised form 25 June 2008
Accepted 27 June 2008

Keywords:
Chlor-alkali
Membrane cell
Brine
Electrolysis
Support vector machine

ABSTRACT

The main aim of this study is to investigate the impacts of operating parameters on the cell performance and predicting the same by SVM technique. This paper though introduces support vector machines (SVMs), a relatively new powerful machine learning method based on statistical learning theory (SLT), into cell voltage and current efficiency forecasting. In order to validate the model predictions, the effects of various operating parameters on the cell voltage and current efficiency of the membrane cell were experimentally investigated. The membrane cell included a standard DSA/Cl_2 electrode as the anode, a nickel electrode as the cathode and a Flemion 892 polymer film as the membrane. Each of six process parameters counting anolyte pH (2–5), operating temperature (25–90 °C), electrolyte velocity (2.2–5.9 cm/s), brine concentration (200–300 g/L), current density (1–4 kA/m^2), and run time were thoroughly studied at four levels for low caustic concentrations (5–22 g/L).

The developed SVM model is not only capable to predict the cell voltage and caustic current efficiency (CCE) but also to reflect the impacts of process parameters on the same functions. The predicted cell voltages and current efficiencies using SVM modelling were found to be very close to the measured values, particularly at higher current densities.

1. Introduction

Chlor-alkali (CA) production is the major industrial scale electro synthesis; total annual capacity of about 55.6 million metric tons of chlorine world-wide [1]. The production of chlorine and caustic soda by electrolysis of aqueous solutions of sodium chloride or brine is one of the most important electrochemical processes, demanding high-energy consumption. The total energy requirement is for instance 2% in the USA and 1% in Japan of the gross electric power generated to maintain this process by the chlor-alkali industry [2,3]. Significant improvement of the electrolytic process in this aspect (i.e., reduction in cell voltage) would be beneficial, both economically and environmentally. Cell voltage and current efficiency are the most important process parameters proportional to the power consumption of a CA plant. Therefore, process evaluation is important from industrial point of view in order to quantify the impact of process variables on these two parameters. At the same time, prediction of the cell voltage and current efficiency can facilitate achieving the optimum conditions as well as reducing the intercalary costs of trial and error experiments.

There are different ways to predict and quantify these parameters such as statistical methods [4], analytical formulations [5] and non-parameter regression methods like artificial neural networks (ANNs) [26] and support vector machine (SVM). However, literature does not show any published work on the application of SVM for such predictions in chlor-alkali industry, though the new SVM methods have already been applied to other fields [6–8].

Statistical methods are used to analyze the results of the experiments and models on response as well as to determine the contribution of each influencing factor. However, the main concern with statistical methods is the difficulties in fulfilling many rigid assumptions that are essential for justifying their applications, e.g. sample size, linearity, and continuity. One alternative approach for system predicting is the technique of SVM based on the structural risk minimization (SRM) principle. Based on this principle, SVM achieves an optimum network structure by striking a right balance between the quality of the approximation of the given data and the complexity of the approximating function. The SVM reveals the underlying statistical relationships among variables corrupted by random error. This SVM algorithm presented by Vapnik [9], as other similar non-parametric statistical regression methods is

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1385-8947/$ – see front matter
doi:10.1016/j.cej.2008.06.030

Nomenclature

C_{brine}	brine concentration (g/L)
E	SVM regression error
F	Faraday's constant (96,458 C/mol); electrolyte velocity (cm/s)
i_p	applied current density (kA/m^2)
I	current (kA)
$K(\cdot,\cdot)$	kernel function
L	Lagrangian function
$m(t=0)$	mass of initial caustic soda, 5 g
$m(t)$	mass of produced caustic at time t (g)
Mw_{NaOH}	caustic molecular weight, 40 g/mol
N	number of exchange mol electron
RBF	redial basis function
t	run time (s)
$X, X_1, \ldots, X_p$	independent or predictor variables
Y	dependent or response variable

Greek letters

γ	parameter for RBF kernel
η_{NaOH}	caustic current efficiency
υ	SVM parameter for performing the cross validation grid search
Φ	transformation for independent variable

intended to alleviate the main drawback of parametric regression, i.e., the mismatch of assumed model structure and the actual data. In nonparametric regression a priori knowledge of the functional relationship between the dependent variable Y and independent variables, X_1, $X_2, \ldots, X_m$, is not required. In fact, one of the main results of non-parametric regression is determination of the actual form of this relationship. The objective of this paper is to develop a general model based on support vector machines to relate the cell voltage and caustic current efficiency (CCE) to operation parameters and quantify the impact of process variables on these two parameters.

SVM is a relatively novel powerful machine learning method based on statistical learning theory (SLT), which is a small sample statistical theory introduced by Vapnik [9]. SVM is powerful for the problems characterized by small samples, nonlinearity, high dimension and local minima. Currently, SVM is an active field in artificial intelligent technology, and has been applied to pattern recognition and function estimation [10]. The empirical risk minimization (ERM) principle is generally employed in the classical methods such as the least-square methods, the maximum likelihood methods and traditional ANN. In SVM, the ERM is replaced by the SRM principle, which seeks to minimize an upper bound of the generalization error rather than minimize the training error [9,11]. Based on this principle, SVM achieves an optimum network structure by striking a right balance between the quality of the approximation of the given data and the complexity of the approximating function. Therefore, the over-fitting phenomenon in general ANN can be avoided and excellent generalization performance can be obtained. Furthermore, in SVM, support vectors corresponding to the hidden units of general ANN are automatically determined after the SVM training. This implies that the difficult task of determining the network structure in general ANN can be prevented. Compared with traditional neural networks, SVM possesses prominent advantages: (1) strong theoretical background provides SVM with high generalization capability and can avoid local minima. (2) SVM always has a solution, which can be quickly obtained by a standard algorithm (quadratic programming). (3) SVM need not determine network topology in advance, which can be automatically obtained when training process ends. (4) SVM builds a result based on a sparse subset of training samples, which reduce the workload.

On the other hand, the CA model achieved by SVM can be employed to examine the effects of various operating parameters as well as to compare the model predictions with the experimental values. With the developed SVM model, one can further study the variations of dependent parameters versus independent parameters. SVM's main difference from statistical methods is attributed to its relinquishment in terms of strict conditions for data samples and associated assumptions. This is applicable to the existing situation of data availability for the cell voltage and CCE factors, which are not good enough for either statistical or numerical modelling. At the same time, analytical models are better than the SVM in terms of their touching the detailed mechanisms of interactions among various impact factors. Nevertheless, such methods' limitations are also from their attempts to specify the complicated processes by detailed mathematical formulations, since many doubtful, interactive, and dynamic system components can barely be expressed as precise analytical formulations. Under such conditions, SVM becomes one of the usable means for analyzing the related effects and interactions; it can be used without disturbing either a number of prerequisites associated with statistical models or being forced to assume unrealistic or over-simplified system conditions that are needed for analytical simulation.

The effects of operating parameters (five factors) on the performance of a CA membrane cell using Taguchi and ANOVA techniques was recently studied by Jalali et al. [4]. However, the effect of electrolysis time was neglected in that study. Besides, to our knowledge, there has been no published literature on SVM modelling of a CA membrane cell. Though, literature have already covered the application of this technique to the modelling of other processes [6–8] and also a previous work of the current authors has developed an ANN model for the prediction of cell voltage and current efficiency in a CA membrane cell [26].

The main aim of this study was thus to investigate the impacts of operating parameters on the cell performance indicators including cell voltage and current efficiency as well as predicting the same by SVM technique. Process parameters that have been studied at four levels include anolyte pH (2–5), cell temperature (25–90 °C), electrolyte velocity (2.2–5.9 cm/s), brine concentration (200–300 g/L), current density (1–4 kA/m^2) and run time (up to 150 min).

2. Theoretical background

2.1. Support vector machines

The problem of empirical data modelling is germane to many engineering applications. In empirical data modelling a process of induction is used to build up a model of the system, from which it is hoped to deduce responses of the system that have yet to be observed. Ultimately the quantity and quality of the observations govern the performance of this empirical model [12]. By its observational nature data obtained is finite and sampled; typically this sampling is non-uniform and due to the high dimensional nature of the problem the data will form only a sparse distribution in the input space. Consequently the problem is nearly always ill posed [13] in the sense of Hadamard [14]. Traditional neural network approaches have suffered difficulties with generalization, producing models that can overfit the data. This is a consequence of the optimization algorithms used for parameter selection and the statistical measures used to select the 'best' model. The foundations of support vector machines have been developed by Vapnik [15] and are gaining popularity due to many attractive features, and promising empirical performance [18]. The formulation embodies the structural risk minimization principle, which has been shown to be superior [16], to traditional empirical risk minimization principle, employed by conventional neural networks. SRM minimizes an upper bound on the expected risk, as opposed to ERM that minimizes the error on the training data. It is this difference which equips SVM with a greater ability to generalize, which is the goal in statistical learning. SVMs were developed to solve the classification problem, but recently they have been extended to the domain of regression problems [17].

2.2. Support vector machine regression

The basic concept of the SVM regression is to map the input data into a feature space via a nonlinear map. In the feature space, a linear decision function is constructed. The SRM principle is employed in constructing optimum decision function. Then SVM nonlinearly maps the inner product of the feature space to the original space via kernels. The SVM nonlinear regression algorithms are reviewed in this section. Given a set of training data

$$(x_1, y_1),\ \ldots,\ (x_l, y_l) \in R^n \times R$$

The nonlinear function φ is employed to map original input space R^n (x element of R^n) to higher dimensional feature space R^k ($\varphi(x)$ element of R^k), where k ($k \gg n$) represents the dimension of feature space. However, this function is not explicitly constructed [27]. Then an optimum decision function $f(x_i) = w^{\mathrm{T}}\varphi(x_i) + b$ is constructed in this higher dimensional feature space, where $w^{\mathrm{T}} = (w_1, \ldots, w_k)$ is a transpose of the vector of weights in this feature space. Nonlinear function estimation in the original space becomes linear function estimation in feature space. By the SRM principle, we obtain the optimization problem:

$$\text{Minimize}\ \ R = \frac{1}{2}||w||^2 + cR_{\mathrm{emp}}$$

where $R_{\mathrm{emp}} = (1/l)\sum_{i=1}^{l} L(y_i, f(x_i))$ is the error term, i.e. empirical risk in learning theory, $||w||^2$ is the regularization term, i.e. confidence interval, which controls the complexity of model [11], and c is a regularization parameter. $L(y_i, f(x_i))$ is the loss function which is the loss or discrepancy between the y to a given input x and goal function $f(x)$. In the SVM regression, $L(y_i, f(x_i))$ is the ε-insensitive loss function, which generally includes the linear ε-insensitive loss function, the quadratic ε-insensitive loss function and the Huber loss function [10]. Different SVM algorithms can be constructed by selecting a different ε-insensitive loss function [12].

2.3. Standard SVM regression algorithm

A linear ε-insensitive loss function is selected in the standard SVM regression. The optimization objective of the standard SVM regression is formulated as

$$\min J(w, \xi) = \frac{1}{2}w^{\mathrm{T}}w + c\sum_{i=1}(\xi_i + \xi_i^*) \tag{1}$$

Subject to

$$\begin{aligned}
&y_i - w^{\mathrm{T}}\varphi(x_i) - b \le \varepsilon - \xi_i,\\
&w^{\mathrm{T}}\varphi(x_i) + b - y_i \le \varepsilon + \xi_i^*,\\
&\xi_i^*, \xi_i \ge 0, \quad i = 1, \ldots, l
\end{aligned}$$

where ξ_i and ξ_i^* are slack variables and ε is the accuracy demanded for the approximation. The solution to this optimization problem is given by the saddle point of the Lagrangian:

$$\begin{aligned}
L(w, \xi^*, \xi, a, a^*, c, \beta, \beta^*) \ =\ & \frac{1}{2}w^{\mathrm{T}}w + c\sum(\xi_i + \xi_i^*)\\
& -\sum_{i=1}^{l} a_i((w^{\mathrm{T}}\varphi(x_i)) - y_i + b + \varepsilon - \xi_i)\\
& -\sum_{i=1}^{l} a_i^*(y_i - (w^{\mathrm{T}}\varphi(x_i)) - b + \varepsilon + \xi_i^*)\\
& -\sum_{i=1}^{l} (\beta\xi_i - \beta_i^*\xi_i^*)
\end{aligned} \tag{2}$$

(Minimum with respect to elements w, b, ξ_i and ξ_i^* and maximum with respect to Lagrange multipliers $a_i \ge 0$, $a_i^* \ge 0$, $\beta_i \ge 0$, $i = 1, \ldots l$). From the optimality conditions

$$\frac{\partial L}{\partial w} = 0, \quad \frac{\partial L}{\partial b} = 0, \quad \frac{\partial L}{\partial \xi_i^*} = 0, \quad \frac{\partial L}{\partial \xi_i} = 0 \tag{3}$$

We have

$$\begin{aligned}
&w^{\mathrm{T}} = \sum_{i=1}^{l}(a_i - a_i^*)\varphi(x_i), \quad \sum(a_i - a_i^*) = 0,\\
&c - a_i - \beta_i = 0, \quad c - a_i^* - \beta_i^* = 0, \quad i = 1, \ldots, l
\end{aligned} \tag{4}$$

Based on the Mercer's condition [10], we define kernels

$$K(x_i, x_j) = \langle\varphi(x_i), \varphi(x_j)\rangle \tag{5}$$

By (2), (4) and (5), the optimization problem can be rewritten as

$$\begin{aligned}
\max W(a, a_i) \ =\ & -\frac{1}{2}\sum_{i=1}^{l}(a_i - a_i^*)(a_j - a_j^*)K(x_i, x_j)\\
& + \sum_{i=1}^{l}(a_i - a_i^*)y_i - \sum_{i=1}^{l}(a_i - a_i^*)\varepsilon
\end{aligned} \tag{6}$$

Subject to

$$\begin{aligned}
&\sum(a_i - a_i^*) = 0\\
&0 \le a_i \le c, \quad i = 1, \ldots, l\\
&0 \le a_i^* \le c, \quad i = 1, \ldots, l
\end{aligned}$$

Finally, nonlinear function is obtained as

$$f(x) = \sum(a_i - a_i^*)K(x_i, x) + b. \tag{7}$$

2.4. Kernels

Kernels $K(x, x_i)$ can be any symmetric function satisfying the Mercer's condition. Different kernels, $K(x, x_i)$, can be selected to construct different types of SVM. Typical examples include [10,12]:

- Polynomial kernels:
  That is a popular method for nonlinear modelling, $K(x, x_i) = [\langle x, x_i\rangle + 1]^d$;
- Radial basis function (RBF) kernels:
  RBFs have received significant attention, most commonly with a Gaussian of the form, $K(x, x_i) = \exp(-((||x - x_i||^2)/2\sigma^2))$;
- Multilayer perceptron kernels:
  The long established MLP, with a single hidden layer, also has a valid kernel representation, $K(x, x_i) = S(\upsilon(x, x_i) + c)$.

In this paper, the RBF function is used as the kernel function of SVM because RBF kernels tend to give good performance under general smoothness assumptions.

3. Experimental

3.1. Materials

The electrolyte was prepared from analytical grade NaCl and NaOH from Merck Inc. (Germany) using double distilled water. All other chemicals used for analysis were also analytical grade.

3.2. Apparatus

The cell performance test was carried out in a CA set-up similar to a scaled-down industrial brine electrolysis unit. Fig. 1 shows a simplified flow diagram of the set-up used in this study.

The cell was a divided filter-press type (Electrocell AB, Sweden) with Flemion® 892 as the separator, a standard DSA Cl_2 and a Ni plate as the anode and the cathode, respectively (see Fig. 2). The electrode membrane gap was 2 mm. The feed tanks were heated by jacketed heaters and their temperature was monitored by digital thermometers. Galvanostatic operation was employed using a DC power supply. Anolyte pH was measured by a pH-meter inserted in the anolyte feed tank. The membrane was immersed in NaOH solution for a day to reach equilibrium prior to each experiment.

3.3. Experimental procedure

The anolyte and catholyte were circulated in separate hydraulic circuits during the experiment by two magnetic pumps according to Fig. 1. The overflows from the anolyte and catholye compartments of the cell were fed to different separators. The bubble free electrolytes were returned to the appropriate feed tanks for further recirculation. During electrolysis, Cl_2 gas produced was absorbed by 2 M NaOH solution in D-03 and then D-04. Constant currents were applied to the cell and the cell voltages were measured. After each test, the set-up was washed thoroughly with distilled water, drained and dried. The electrolysis run times were either of 30, 60, 90, 120 and 150 min.

3.4. Chemical analysis

In order to measure the caustic produced, catholyte samples were collected from D-02 and titrated against 0.1 N HCl. These data were then used for calculation of the caustic current efficiency.

3.5. SVM modelling

As mentioned before, the SVM algorithm was applied to correlate the cell voltage and CCE to the independent variables of pH, current density, temperature, flow rate, brine concentration and run time.

Various SVM architectures were investigated to obtain desired model for predicting cell performance as a function of selected input variables. Different scenarios on the type of kernel (polynomial, linear, radial basis function (RBF), or sigmoid), and kernel parameters (degree, gamma, coefficient) were analyzed to obtain the best fit to the given data. Therefore, the developed model using the SVM algorithm was designed to reach the optimal regression between input variables.

Usually, in the training phase, a larger part of data (75%) was used to train the model. To validate the model, 25% data pairs were used for the testing purpose.

The performances of the SVM models were compared using the root mean square error (RMSE), correlation coefficient, R^2, and T statistics Eq. (8). T value measures the scattering around the line (1:1). Where T is close to 1.0, a good fitting is prevailed.

$$\mathrm{RMSE}=\sqrt{\frac{1}{n}\sum_{i=1}^{n}(X_{\mathrm{im}}-X_{\mathrm{ip}})^2},\qquad T=1-\frac{\sum_{i=1}^{n}(X_{\mathrm{im}}-X_{\mathrm{ip}})^2}{\sum_{i=1}^{n}(X_{\mathrm{im}}-\bar{X})^2} \tag{8}$$

where n is the number of data points, $\bar{X}$ the average of X over the n samples, and X_{im} and X_{ip} are the measured and predicted values of process and product parameters, respectively. The final model was selected on the basis of the lowest error on train and test sets of data. Meanwhile, the accuracy of the SVM models was evaluated by calculating standard deviation (S.D.) and average deviation (AD) for each of the outputs for testing. A lower S.D. and AD indicate a better prediction. S.D. and AD were calculated as

$$\mathrm{S.D.}=\sqrt{\frac{\sum_{i=1}^{n}[((|X_{\mathrm{im}}-X_{\mathrm{ip}}|)/X_{\mathrm{im}})\times 100]^2}{n-1}},$$

$$\mathrm{AD}=\frac{1}{n}\sum_{i=1}^{n}\frac{|X_{\mathrm{im}}-X_{\mathrm{ip}}|}{X_{\mathrm{im}}}\times 100 \tag{9}$$

Different algorithms were made and the optimum values of kernel parameters obtained by trial and error. Adjustment of SVM parameters included the kernel type, SVM type, kernel parameters, υ, γ and number of support vectors. υ and γ are SVM parameter for performing the cross validation grid search and parameter for RBF kernel, respectively.

4. Results and discussions

4.1. Data collection

The important parameters affecting the CA cell performance based on our experiences and previous works [4,19–24] along with the levels of these parameters are as follows: (1) anolyte pH: 2, 3, 4 and 5, (2) cell temperature (°C): 25, 50, 70 and 90, (3) flow velocity (cm/s): 1.3, 2.2, 3.7 and 5.9, (4) brine concentration (g/L): 200, 235, 270 and 300, (5) current density (kA/m^2): 1, 2, 3 and 4 and (6) run time: from 30 to 150 min. The latter are summarized in Table 1.

By conducting experiments under these conditions using the previously mentioned procedure, cell voltage and CCE data were obtained.

4.2. Calibration and developing cell voltage and CCE model

The cell voltage and CCE data were divided into two data sets, consisting of training and validation test data. In the training phase, a larger part of data (75%) was used to train the models and the remaining data (25%) were used in the validation phase. The main aim of this activity was to obtain an SVM model with a minimal dimension and minimum errors in training and testing calculations. Different scenarios on the type of kernel and kernel parameters were analyzed to obtain the best fit to the given data. For this structure, the best combination of the SVM and kernel parameters that were used to predict the cell voltage and CCE is shown in Table 2.

Scatter data of Figs. 3 and 4 (a and b) provide comparisons of the measured cell voltage and CCE levels with those of SVM-derived test and train calculations. Tables 3 and 4 also give the overall outputs of experiments and the results obtained based on the SVM model predictions for cell voltage and CCE. According to these results, both data sets provide a low average deviation (AD) among experimental data and SVM model predictions. However, the results of developed

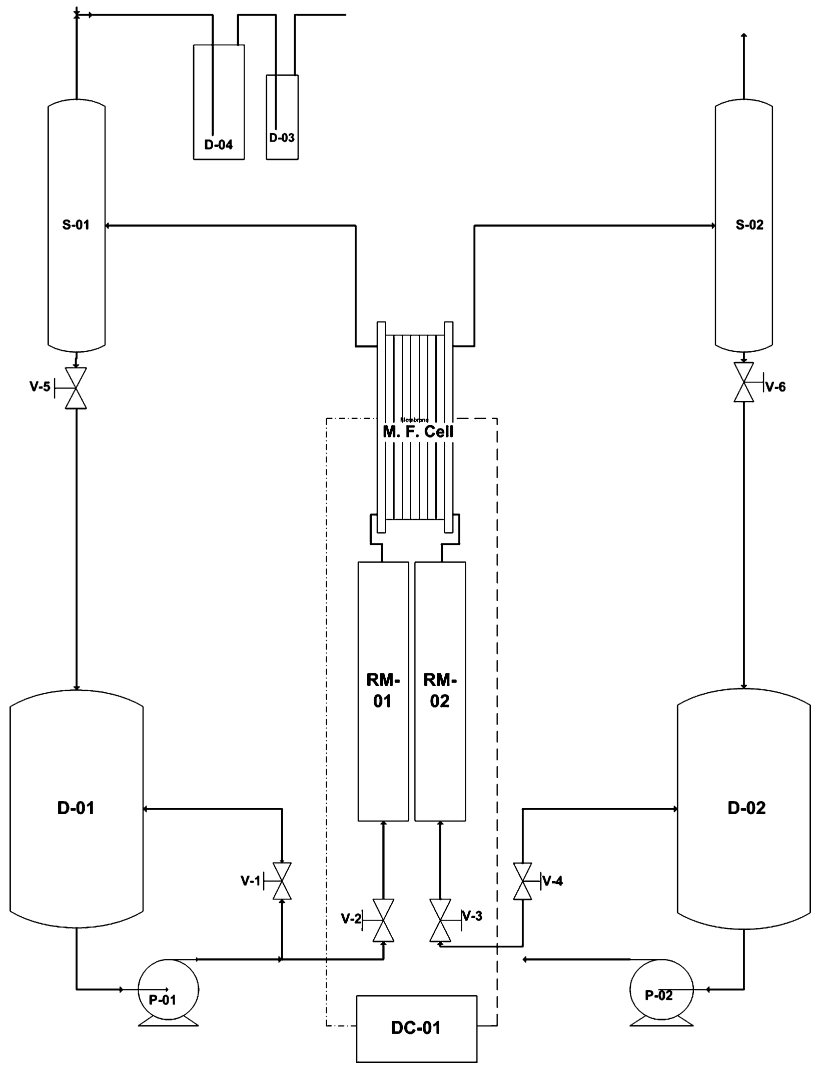

Fig. 1. Process flow diagram of the chlor-alkali set-up utilized: (1) Membrane flow cell (M.F. cell). (2) Electrolyte tank (D-01, D-02). (3) Magnetic pumps (p-01, P-02). (4) Gas separator (S-01, S-02). (5) Rotameter (RM-01, RM-02). (6) DC power supply. (7) Two feed tank consist of NaOH for neutralization produced chlorine (D-03, D-04).

Table 1
Levels of process parameters

	pH	Cell temperature (°C)	Flow velocity (cm/s)	Brine concentration (g/L)	Current density (kA/m^2)	Run time (min)
Level 1	2	25	1.3	200	1	30
Level 2	3	50	2.2	235	2	60
Level 3	4	70	3.7	270	3	120
Level 4	5	90	5.9	300	4	150

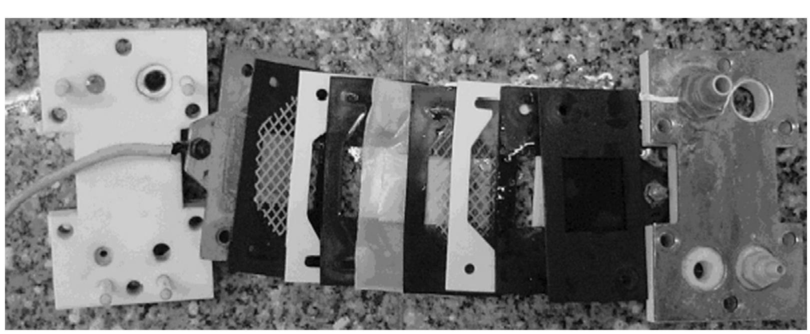

Fig. 2. Side view of the membrane cell used in this study. (1) Cell body (Teflon). (2) EPDM gasket. (3) Standard DSA/Cl_2 anode. (4) Flemion 892 membrane. (5) Nickel cathode. (6) Flow frame (Teflon). (7) Electrolyte inlet. (8) Electrolyte outlet, respectively.

Table 2
The structure and performance of the final selected SVM model with optimum values of model parameters used to predict (a) cell voltage and (b) CCE

Optimum				Mean value				
Kernel type	υ	γ	Number of support vectors	Training		Testing		T
				RMSE	R^2	RMSE	R^2	
(a) RBF	0.54	0.46	38	0.118	0.995	0.161	0.988	0.992
(b) RBF	0.5	0.58	48	0.009	0.966	0.016	0.873	0.939

SVM model for cell voltage have a lower dispersion compared with that of CCE which is likely to be due to the titration errors. This implies that the developed SVM model in this study can accurately forecast the cell voltage and CCE values.

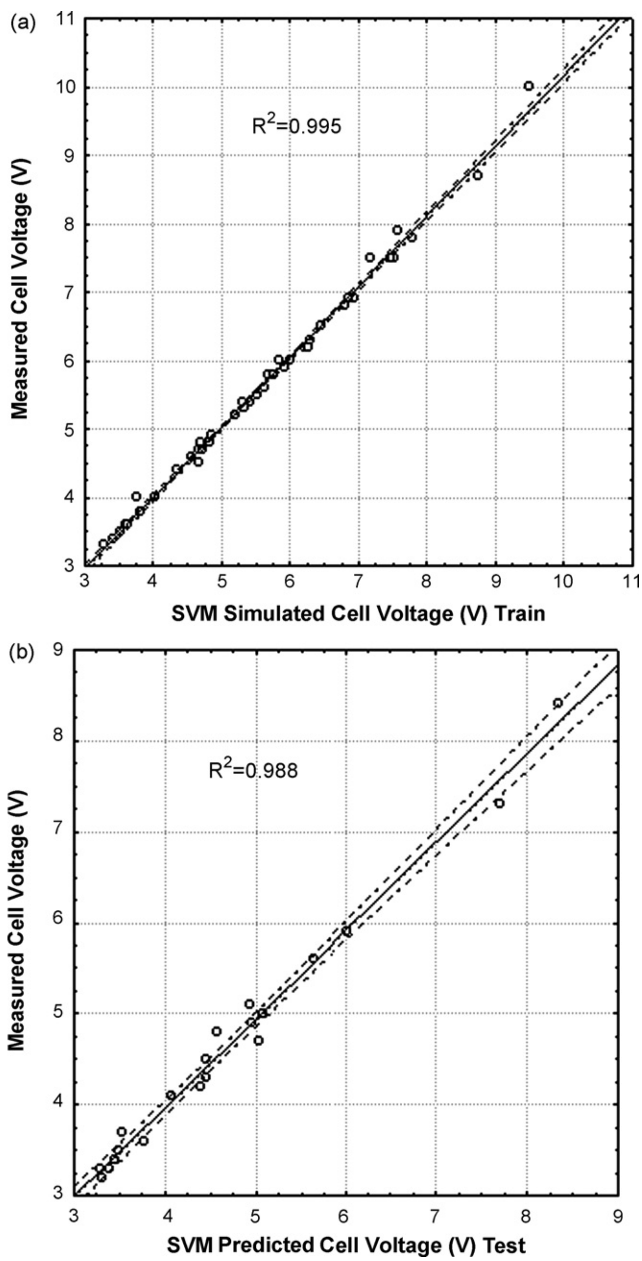

Fig. 3. The measured versus SVM-simulated for cell voltage. (a) Train and (b) test values within 95% accuracy.

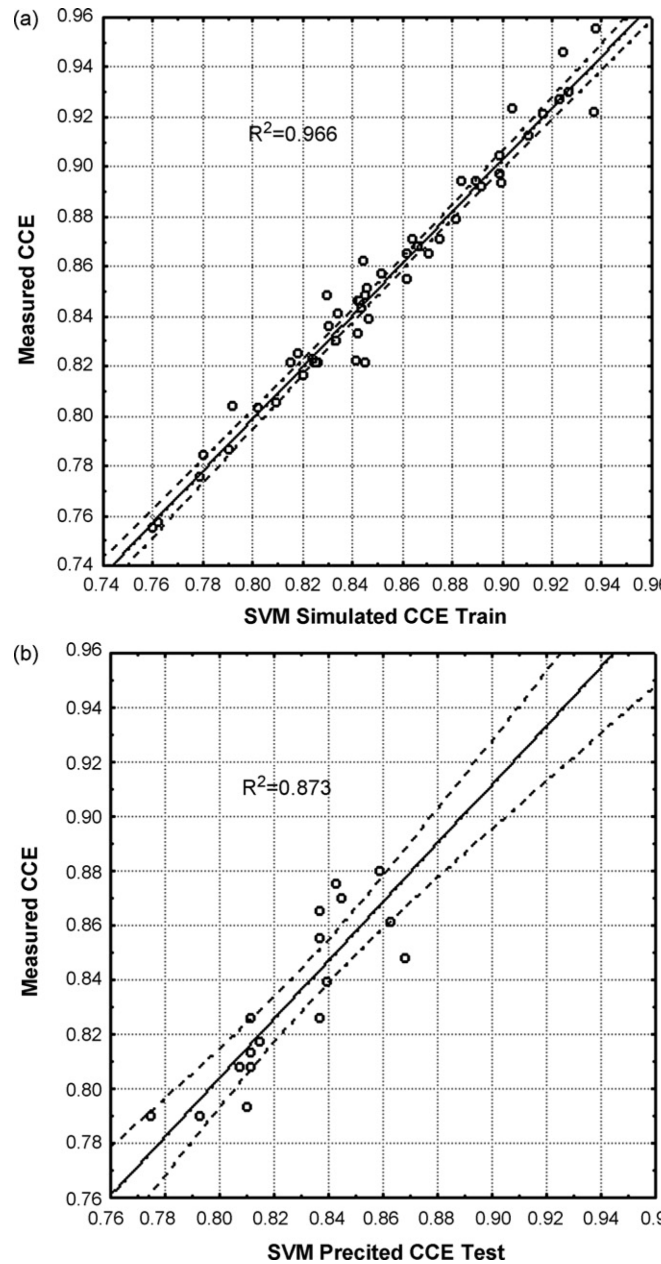

Fig. 4. The measured versus SVM-simulated for CCE. (a) Train and (b) test values within 95% accuracy.

4.3. Sensitivity analysis

Model sensitivity to each of the inputs is given by:

$$\text{Sensitivity} = \frac{\%\,\text{change in output}}{\%\,\text{change in input}} \times 100 \tag{10}$$

This relates the change in output for a change of a given input. Eq. (10) shows the relative importance of an individual parameter for a given input set. A variable having a high sensitivity is most likely important to the modeled process. The sensitivity was calculated for each of the input parameters. A graphical and quantitative presentation of the impacts of the operating parameters with contribution of each factor on mean response for experimental and SVM-simulated cell voltage and current efficiency are compared in Figs. 5 and 6. First of all, it is obvious that the SVM model predictions are very close to the experimental

Table 3
Experimental and SVM-simulated cell voltage values

Time (min)	pH	Temperature (°C)	Flow (cm/s)	Brine concentration (g/L)	Current density (kA/m^2)	Exp. cell voltage (V)	SVM-Pred. Voltage (V)	Error (%)
30	4	50	5.9	270	1	3.6	3.76	4.55
30	5	70	2.2	300	1	3.7	3.54	4.34
30	3	90	3.7	235	1	3.8	3.80	0.13
30	2	50	2.2	235	2	4.7	5.03	7.00
30	3	70	5.9	200	2	4.8	4.81	0.27
30	5	90	1.3	270	2	4.8	4.83	0.62
30	2	25	1.3	200	1	5.2	5.20	0.04
30	4	25	3.7	300	2	5.6	5.62	0.40
30	2	70	3.7	270	3	5.9	6.01	1.91
30	4	90	2.2	200	3	6.0	6.00	0.05
30	3	50	1.3	300	3	6.8	6.80	0.05
30	2	90	5.9	300	4	7.5	7.18	4.33
30	4	70	1.3	235	4	7.8	7.79	0.07
30	5	25	5.9	235	3	7.9	7.58	4.02
30	5	50	3.7	200	4	8.4	8.35	0.54
30	3	25	2.2	270	4	10.0	9.50	5.00
60	4	50	5.9	270	1	3.5	3.51	0.23
60	5	70	2.2	300	1	3.5	3.50	0.10
60	3	90	3.7	235	1	3.6	3.61	0.21
60	3	70	5.9	200	2	4.4	4.35	1.12
60	2	50	2.2	235	2	4.6	4.57	0.68
60	5	90	1.3	270	2	4.7	4.66	0.80
60	2	25	1.3	200	1	5.1	4.94	3.16
60	2	70	3.7	270	3	5.3	5.34	0.71
60	4	25	3.7	300	2	5.4	5.30	1.82
60	4	90	2.2	200	3	5.4	5.42	0.43
60	2	90	5.9	300	4	6.2	6.23	0.41
60	3	50	1.3	300	3	6.2	6.27	1.16
60	4	70	1.3	235	4	6.9	6.94	0.56
60	5	25	5.9	235	3	6.9	6.85	0.68
60	5	50	3.7	200	4	7.5	7.53	0.35
60	3	25	2.2	270	4	8.7	8.74	0.43
120	3	90	3.7	235	1	3.3	3.39	2.82
120	4	50	5.9	270	1	3.3	3.29	0.45
120	5	70	2.2	300	1	3.4	3.45	1.50
120	3	70	5.9	200	2	4.0	3.76	5.90
120	2	50	2.2	235	2	4.1	4.08	0.50
120	5	90	1.3	270	2	4.3	4.46	3.79
120	2	25	1.3	200	1	4.6	4.57	0.70
120	2	70	3.7	270	3	4.7	4.67	0.59
120	4	90	2.2	200	3	4.8	4.69	2.19
120	4	25	3.7	300	2	4.9	4.85	0.93
120	2	90	5.9	300	4	5.0	5.08	1.58
120	3	50	1.3	300	3	5.6	5.63	0.51
120	4	70	1.3	235	4	6.0	5.85	2.55
120	5	25	5.9	235	3	5.9	5.91	0.22
120	5	50	3.7	200	4	6.5	6.46	0.59
120	3	25	2.2	270	4	7.3	7.70	5.45
150	3	90	3.7	235	1	3.2	3.32	3.75
150	4	50	5.9	270	1	3.3	3.27	0.99
150	5	70	2.2	300	1	3.4	3.40	0.14
150	3	70	5.9	200	2	3.6	3.62	0.62
150	2	50	2.2	235	2	4.0	4.02	0.48
150	5	90	1.3	270	2	4.2	4.40	4.82
150	2	70	3.7	270	3	4.5	4.66	3.51
150	2	25	1.3	200	1	4.5	4.45	1.12
150	4	25	3.7	300	2	4.7	4.71	0.28
150	4	90	2.2	200	3	4.8	4.57	4.87
150	2	90	5.9	300	4	4.9	4.95	1.08
150	3	50	1.3	300	3	5.5	5.51	0.23
150	4	70	1.3	235	4	5.8	5.68	2.10
150	5	25	5.9	235	3	5.8	5.75	0.79
150	5	50	3.7	200	4	6.3	6.29	0.11
150	3	25	2.2	270	4	7.5	7.47	0.35
							AD = 1.59%	

data. Current density has the most prominent effect on the cell voltage as seen in Fig. 5 with a effect value of 55.4% while the temperature and run time are the second and third influencing parameters with a effect value of about 21.7 and 17.8%, respectively. Brine concentration has the lowest effect with impact values of less than 1%. The impacts of pH and flow rate on the cell voltage are comparable and quite low within the experimental range studied.

Brine concentration and temperature are important parameters for control of CCE according to Fig. 6. However, in respect to CCE, the effects of operating parameters, more or less, are of the same order. Here, brine concentration has the highest impact with effect

Table 4
Experimental and SVM-simulated CCE values

Time (min)	pH	Temperature (°C)	Flow (cm/s)	Brine concentration (g/L)	Current density (kA/m^2)	Exp. CCE	SVM-Pred. CCE	Error (%)
29	4	25	3.7	300	2	0.861	0.863	0.23
30	5	70	2.2	300	1	0.865	0.837	3.24
30	5	50	3.7	200	4	0.894	0.890	0.44
30	2	25	1.3	200	1	0.904	0.899	0.53
30	3	70	5.9	200	2	0.912	0.911	0.15
30	2	90	5.9	300	4	0.897	0.899	0.21
30	3	25	2.2	270	4	0.843	0.844	0.07
31	4	90	2.2	200	3	0.862	0.844	2.05
31	2	70	3.7	270	3	0.823	0.824	0.12
31	3	90	3.7	235	1	0.963	0.945	1.92
31	4	70	1.3	235	4	0.755	0.760	0.65
31	4	50	5.9	270	1	0.921	0.916	0.49
50	3	50	1.3	300	3	0.803	0.802	0.11
60	3	25	2.2	270	4	0.822	0.842	2.38
60	3	90	3.7	235	1	0.930	0.927	0.36
60	4	90	2.2	200	3	0.821	0.826	0.66
60	4	25	3.7	300	2	0.857	0.852	0.56
60	2	90	5.9	300	4	0.946	0.925	2.25
60	3	70	5.9	200	2	0.892	0.892	0.03
61	5	90	1.3	270	2	0.808	0.807	0.07
61	5	70	2.2	300	1	0.830	0.834	0.46
61	4	50	5.9	270	1	0.893	0.900	0.76
61	2	70	3.7	270	3	0.836	0.830	0.66
61	5	25	5.9	235	3	0.786	0.791	0.59
61	2	25	1.3	200	1	0.848	0.868	2.41
61	4	70	1.3	235	4	0.757	0.762	0.73
90	5	25	5.9	235	3	0.775	0.779	0.47
90	3	90	3.7	235	1	0.923	0.904	2.01
90	4	25	3.7	300	2	0.848	0.845	0.29
90	3	70	5.9	200	2	0.871	0.875	0.48
90	2	25	1.3	200	1	0.821	0.845	2.95
90	4	50	5.9	270	1	0.894	0.884	1.10
90	2	90	5.9	300	4	0.955	0.938	1.77
91	5	70	2.2	300	1	0.841	0.834	0.80
91	3	25	2.2	270	4	0.846	0.843	0.40
91	5	90	1.3	270	2	0.826	0.811	1.77
91	4	90	2.2	200	3	0.817	0.815	0.27
91	2	70	3.7	270	3	0.855	0.837	2.08
91	5	50	3.7	200	4	0.855	0.862	0.80
92	4	70	1.3	235	4	0.790	0.775	1.87
100	3	50	1.3	300	3	0.813	0.811	0.20
120	2	70	3.7	270	3	0.833	0.842	1.12
120	2	90	5.9	300	4	0.922	0.937	1.60
120	3	70	5.9	200	2	0.871	0.864	0.80
120	5	25	5.9	235	3	0.784	0.780	0.50
120	4	25	3.7	300	2	0.875	0.843	3.68
120	3	25	2.2	270	4	0.870	0.845	2.91
120	4	50	5.9	270	1	0.865	0.871	0.68
121	5	90	1.3	270	2	0.825	0.818	0.85
121	4	70	1.3	235	4	0.804	0.792	1.47
121	3	90	3.7	235	1	0.879	0.882	0.29
121	5	70	2.2	300	1	0.826	0.837	1.31
121	4	90	2.2	200	3	0.808	0.812	0.47
122	2	25	1.3	200	1	0.848	0.830	2.15
150	3	25	2.2	270	4	0.839	0.846	0.89
150	4	70	1.3	235	4	0.805	0.810	0.58
150	4	90	2.2	200	3	0.821	0.815	0.69
150	5	25	5.9	235	3	0.790	0.793	0.41
150	5	50	3.7	200	4	0.868	0.866	0.21
150	3	70	5.9	200	2	0.880	0.859	2.36
150	5	90	1.3	270	2	0.821	0.825	0.45
150	2	50	2.2	235	2	0.793	0.810	2.20
150	2	70	3.7	270	3	0.851	0.846	0.59
150	5	70	2.2	300	1	0.839	0.840	0.10
150	4	25	3.7	300	2	0.846	0.843	0.33
150	3	50	1.3	300	3	0.816	0.821	0.56
150	4	50	5.9	270	1	0.865	0.862	0.34
150	2	90	5.9	300	4	0.927	0.924	0.37
150	2	25	1.3	200	1	0.821	0.825	0.54
							AD = 0.98%	

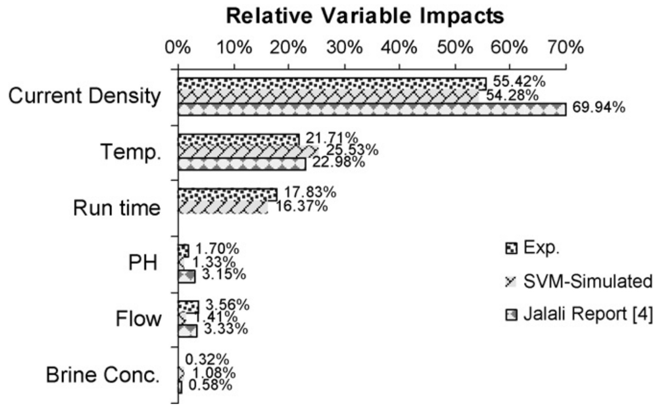

Fig. 5. Sensitivity analysis results based on this work, Jalali's experimental [4] and SVM-simulated cell voltage results.

value of 20.36% while the lowest impact corresponds to flow with effect value of 10.6%.

Also for comparison purposes, the experimental and SVM results from this study were compared with those obtained by Jalali et al. [4] in these figures. These graphs compare sensitivity analysis for five parameters without run time input from Jalali's data. Although they neglected the influence of run time, but their results are in good agreement with our experimental and thus SVM model outputs. Finally it can be realized that current density and brine concentration variables have the highest impacts on the CA cell voltage and CCE, respectively.

4.4. Effect of operating parameters on the cell performance indicators

Based on SVM outputs, the effect of controllable operating parameters on the mean response for the CA cell voltage and CCE are displayed in Figs. 7–12. According to these results, cell voltage is enhanced dramatically with current density while it is altered slightly with the anolyte pH. On the other hand, the cell voltage significantly decreases with increasing the cell temperature while slightly with those of flow rate and brine concentration. The cell voltage also decreases with run time.

The conditions to obtain a minimum value for cell voltage simulated by SVM model are as follows: pH (2), T (90 °C), flow (5.9 cm/s), C_{brine} (300 g/L), i_p (1 kA/m^2) and the run time (150 min).

Another valuable response which is directly proportional to the total energy consumed by an electrolysis cell is the current efficiency. The caustic current efficiency was thus measured according to the procedure described in Section 3 and calculated based on the

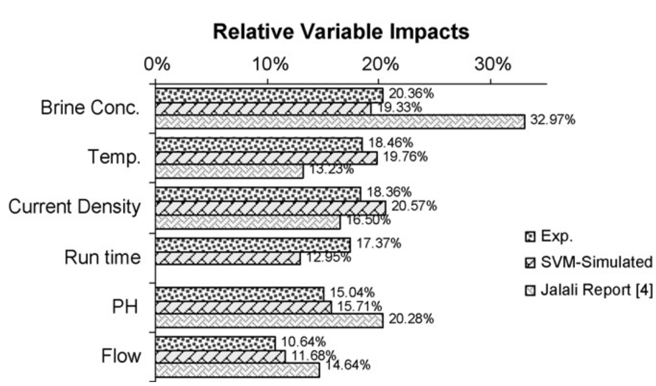

Fig. 6. Sensitivity analysis results based on this work, Jalali's experimental [4] and SVM-simulated CCE results.

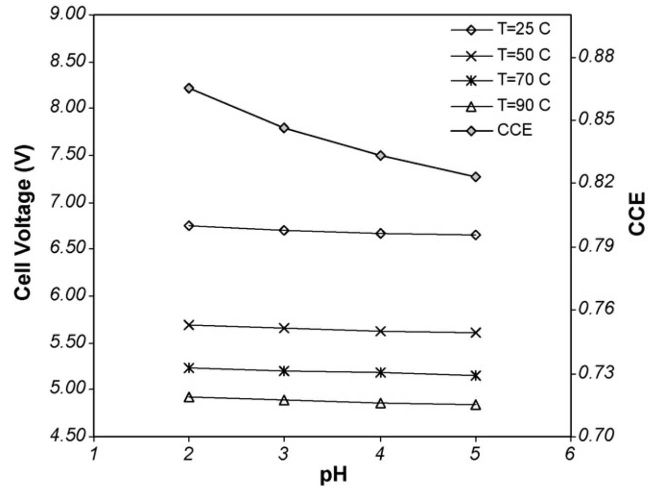

Fig. 7. Cell voltage and current efficiency at different levels of pH resulted from the new SVM based model.

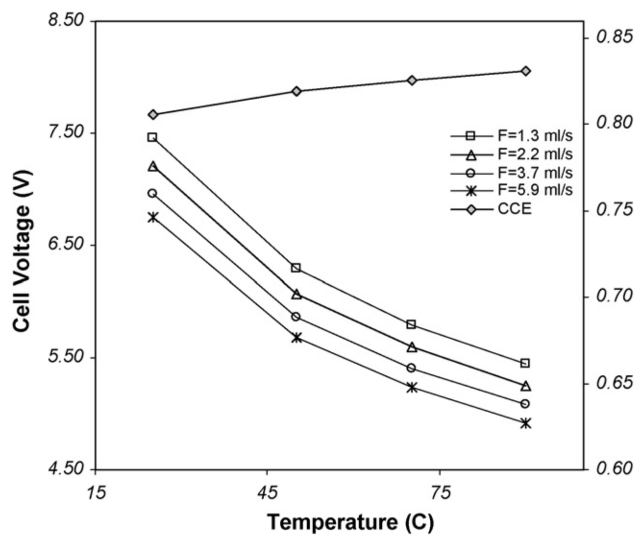

Fig. 8. Cell voltage and current efficiency at different levels of temperature by the new SVM based model.

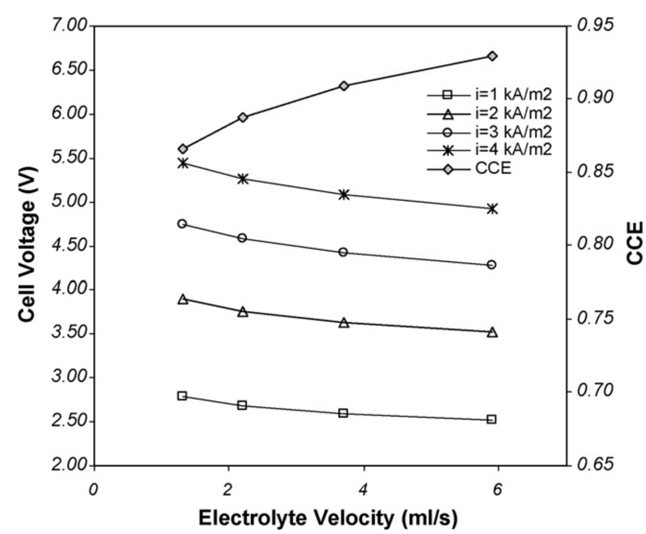

Fig. 9. Cell voltage and current efficiency at different levels of electrolyte velocity by the new SVM based model.

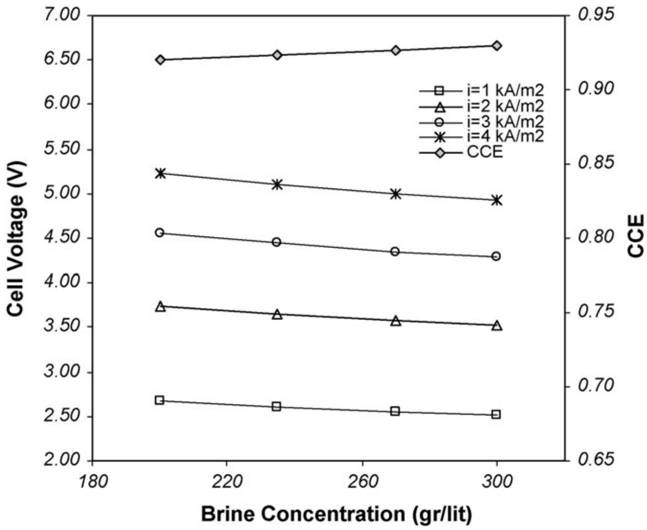

Fig. 10. Cell voltage and current efficiency at different levels of brine concentration by the new SVM based model.

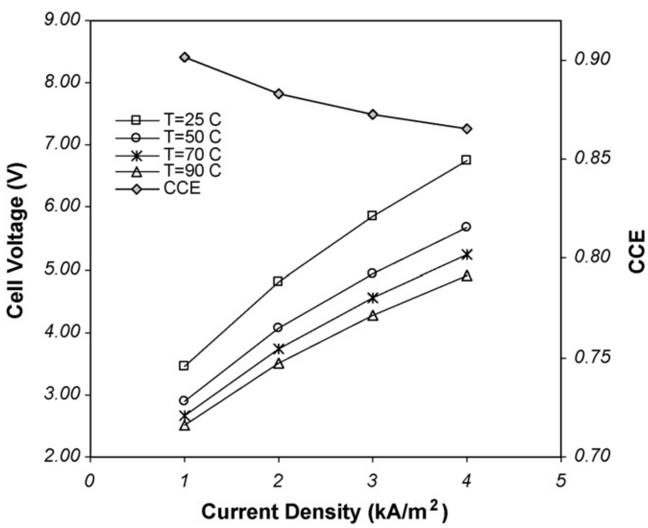

Fig. 11. Cell voltage and current efficiency at different levels of current density by the new SVM based model.

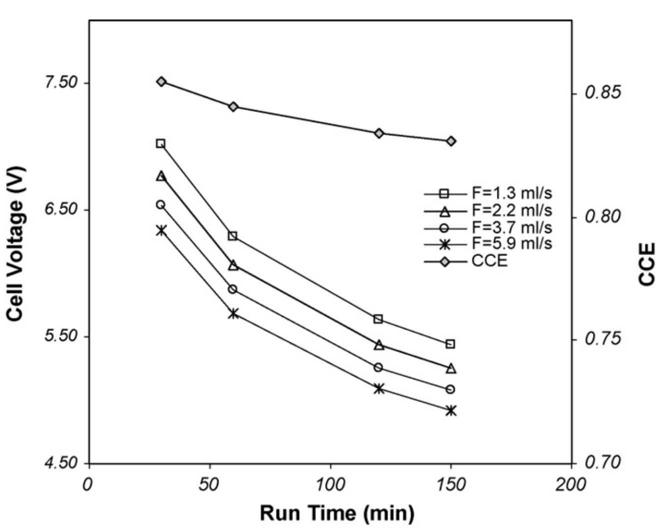

Fig. 12. Cell voltage and current efficiency at different levels of run time by the new SVM based model.

following equation [25]:

$$\eta_{\text{NaOH}} = \frac{m(t) - m(t=0)}{(It/nF) \times \text{Mw}_{\text{NaOH}}} = \frac{m(t) - m(t=0)}{(It/nF) \times 40} \tag{11}$$

The impacts of various operating parameters on the CCE, based on SVM results, are shown in Figs. 7–12.

According to Fig. 7, the current efficiency decreases with pH due to the production of by products such as hypochlorite and chlorate in anolyte at higher pH's while pH does not have a sensible impact on the CA cell voltage.

Fig. 8 shows variation of the caustic current efficiency and cell voltage with the cell temperature. As it is seen, CCE improves with cell temperature due to depressing of the side reactions while the overall cell voltage decreases with temperature because of a decrease in the voltage components of the cell such as decomposition potential, IR drops and the overpotentials.

By increasing electrolyte velocity, a slight decrease in the cell voltage can be observed as shown in Fig. 9. This may be caused by a reduction in the amount of attached H_2 and Cl_2 bubbles on both sides of the membrane and the bubbles remained within the catholyte and anolyte [21,24]. The presence of the bubbles decreases the actual conductivity of the electrolyte and thus it increases cell voltage.

The cell voltage is also decreases slightly with brine concentration within the brine concentration range studied, but the effect of brine concentration on current efficiency is pronounced, as seen in Fig. 10. This is likely to be due to suppressing of the oxygen evolution as a major side reaction at low brine concentration.

According to Fig. 11 the current density was discovered to be the most remarkable parameter influencing the cell voltage and current efficiency. These facts were expected considering the ohms law for the cell voltage ($\Delta V_{\text{Cell}} = I \times R_{\text{Cell}}$); and Eq. (11) describing the inverse relationship between current density and CCE.

Both functions have a downtrend with increasing run time according to Fig. 12. The lower CCE achieved at higher run times. In other words, the higher caustic concentration may be due to the OH^- back migration toward anolyte at higher runtimes. The catholyte conductivity enhances with NaOH concentration within the caustic concentration range studied resulting in a decrease in the cell voltage.

For comparison purposes, the results from Jalali et al. [4] for an experimental system similar to the one used in this study but at different conditions, are also represented in Fig. 13. As it is obvious, the general prediction trends developed in this study by the SVM model are quite consistent with the experimental results and trends obtained by Taguchi and ANOVA techniques used [4]. Nevertheless, a slight difference in values is observable due to the differences in the set-up conditions as well as neglecting the run time as a parameter in that study.

On the other hand for comparison between two different non-parameter regression methods, the ANN modelling results from Shojai Kaveh et al. [26] for this experimental system, along with the results of SVM model are shown in Table 5. According to this table, ANN model for cell voltage has better consistency with exper-

Table 5
Comparison between the predictions of ANN & SVM models for the same experimental data

	Cell voltage			CCE		
	AD%	R^2 (train)	R^2 (test)	AD%	R^2 (train)	R^2 (test)
SVM model (this work)	1.59	0.995	0.966	0.98	0.988	0.873
ANN model [26]	1.27	0.997	0.989	3.14	0.903	0.802

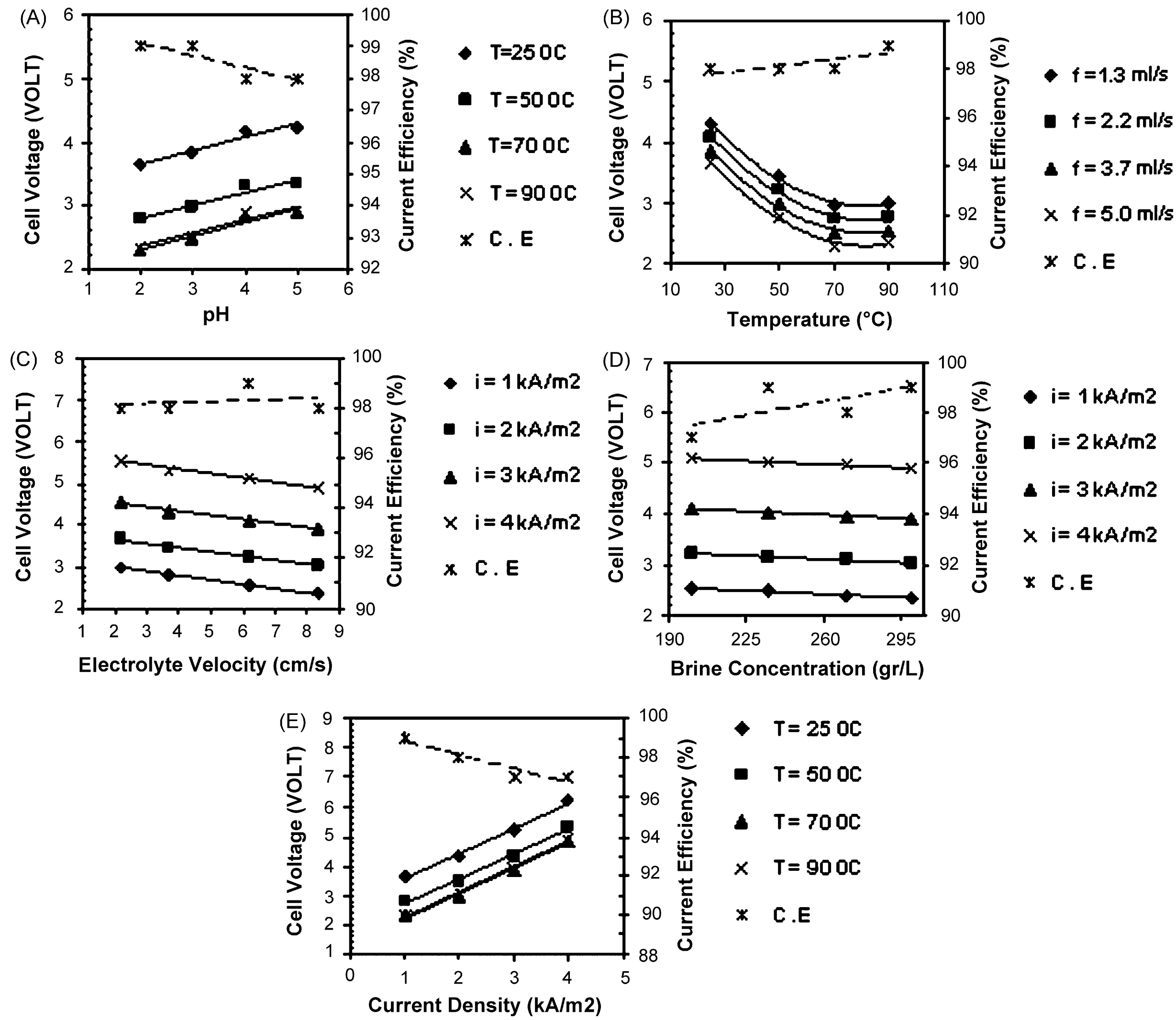

Fig. 13. Cell voltage and current efficiency at different levels of operating parameters, (A) pH, (B) temperature, (C) electrolyte velocity, (D) Brine concentration, and (E) current density [4].

imental data and also the results of SVM model has a lower average error for predicting CCE.

5. Conclusions

Cell voltage and caustic current efficiency are widely employed to improve or enhance the performance of chlor-alkali membrane cells. Therefore, accurate prediction of CCE and cell voltage is of utmost importance. In this study a new SVM model for the prediction of cell voltage and CCE was developed. The effectiveness of the developed SVM model was also validated by comparing the predicted results with the measured cell voltage and CCE values. Based on the results obtained in this study, the following conclusions are drawn:

1. SVM model can be used to predict the impacts of operating parameters including pH, temperature, flow rate, brine concentration, current density and run time on the cell voltage and current efficiency of a chlor-alkali cell.
2. The SVM technology has been shown to be a useful tool not only to approximate but also to predict cell voltage and CCE versus process parameters in membrane chlor-alkali cell.
3. The final selected SVM models were able to predict the cell voltage and CCE values with RMSE of 0.161 and 0.016, R^2 of 0.998 and 0.873, and T values of 0.992 and 0.939, respectively.
4. The current density and cell temperature have the highest effect values on the cell voltage, i.e. 55.4 and 21.7%, respectively.
5. Based on SVM-simulated outputs, the following operating conditions are proposed to maximize the current efficiency and minimize the cell voltage: pH = 2; temperature = 90 °C; flow rate = 5.9 cm/s; brine concentration = 300 g/L; and current density = 1 kA/m^2.
6. Evaluation of the relative effectiveness of operating parameters by the SVM model revealed that while current density and temperature have the largest contribution to the cell voltage, brine concentration have the largest impact on the current efficiency. Other factors have almost similar effects on the response.
7. The values of predicted cell voltages and CCE were quite comparable with those of measured values with an average deviation of only 1.59 and 0.98%, respectively.
8. A comparison between SVM model of this work and ANN model from a previous work [26] shows that the developed ANN model predicts the cell voltage, and the developed SVM model predicts current efficiency, more accurately.

Acknowledgement

National Petrochemical Research and Technology Company of Iran (NPC-RT) is highly acknowledged for its financial support.

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