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Research Article

BROMATE REMOVAL PREDICTION IN DRINKING WATER BY USING THE LEAST SQUARES SUPPORT VECTOR MACHINE (LS-SVM)

Erdal KARADURMUŞ*[1], Eda GÖZ[2], Nur TAŞKIN[3], Mehmet YÜCEER[4]

[1]*Chemical Engineering Department, Hitit University, ÇORUM;* ORCID: 0000-0002-1836-5126
[2]*Chemical Engineering Department, Ankara University, ANKARA;* ORCID: 0000-0002-3111-9042
[3]*Chemical Engineering Department, Hitit University, ÇORUM;* ORCID: 0000-0002-9268-6649
[4]*Chemical Engineering Department, İnönü University, MALATYA;* ORCID: 0000-0002-2648-3931

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ABSTRACT

The main objective of this study was to develop Least Squares Support Vector Machine (LS-SVM) algorithm for prediction of bromate removal in drinking water. Adsorption method known as environmental-friendly and economical was used in the experimental part of this study to remove this harmful compound from drinking water. Technically (pure), HCl-, NaOH- and NH_3-modified activated carbons were prepared as adsorbent. Experimental studies were carried out with synthetic samples in three different concentrations. To forecast bromate removal percentage particle size and amount of the activated carbon, height and diameter of the column, volumetric flowrate, and initial concentration were selected as the input variables Radial basis kernel function was selected as activation function in algorithm. Algorithm parameters that γ and σ^2 values set as 415 and 3.956 respectively. To evaluate model performance some performance indices were calculated. Correlation coefficient (R), mean absolute percentage error (MAPE%) and root mean square error (RMSE) value for the training and testing phase R:0.996, MAPE%: 2.59 RMSE: 2.14 and R:0.994, MAPE%: 3.21 RMSE: 2.51 respectively. These results obtained from this study were compared with the ANN model previously developed with the same input data. As a result, LS-SVM has better performance than ANN.
Keywords: Drinking water treatment, bromate removal, artificial intelligence, LS-SVM.

1. INTRODUCTION

Rapid increase in population with the increase in agricultural and industrial activities in recent years threatens water resources seriously. Within the scope of disinfection of natural water sources, chlorination, ozonation and ultraviolet radiation methods are frequently used. In ozonation and disinfection studies, bromide ion in drinking and domestic waters turns into bromate ion, which has a carcinogenic effect. This disinfection by-product (DYU) is known as a group 2B carcinogenic substance. According to the World Health Organization (WHO) criteria, its acceptable value has been determined as 10µg/L [1, 2]. Various adsorption columns, anaerobic bacteria, coagulation and membrane reactors are used for removal of disinfection by-products. Among these methods, adsorption process is known as environmental friendly and economical [3]. Although there are many articles in the literature where experimental studies on bromate

* Corresponding Author: e-mail: erdalkaradurmus@hitit.edu.tr, tel: (364) 227 45 33 / 1264

removal using adsorption processes are published, modeling studies of drinking water are quite limited. Experimental studies using small and pilot scale adsorption columns are included in the literature [4]. In this context, active carbons in granule and powder form have been used in bromate removal studies. Besides, modified activated carbon structures are also prepared to increase the adsorption capacity of activated carbons of different structures. activated carbon is obtained from different biomass sources [5]. In this context, research was conducted on bromate ion removal capacities of wood-based carbon, fruit-based carbon, coal-based carbon [5]. These carbon samples were prepared under the nitrogen atmosphere via deoxidizing with temperature. Among the samples obtained that coal-based activated carbon has better adsorption capacity due to its high zeta potential and porosity. In another study examining the effect of surface modification on adsorption capacity, granular activated carbon was modified in the presence of a cationic surfactant CTAC (cetyltrimethylammonium ammonium chloride) [6]. According to the results of adsorption isotherms and kinetic studies, the adsorption capacity of activated carbon increased in the presence of CTAC. The effect of empty column contact time (EBCT) was investigated in a pilot scale study to remove bromate ions formed as a result of ozone of packaged drinking water of granular active carbons [7]. In the study, it was determined that as the empty column contact time increased, bromate removal increased. In Naushad's study [3] of the biomass palm kernel with H_3PO4, activated carbon was synthesized by chemical activation process and the effects of parameters such as pH, equilibration time, first bromate concentration and temperature on bromate adsorption were investigated. In order to increase the capacity of bromate adsorption, active carbon structures modified with polyprol were prepared in Hong's study [8]. At the end of the study, a significant increase in adsorption capacity was observed due to the presence of positively charged pyrrolic-N groups on the activated carbon surface.

When the studies in the literature are examined, it has been observed that activated carbon and its modified structures are frequently used in bromate removal. However, the prediction of bromate removal with modeling techniques is limited. Artificial neural network model and multivariate regression models for removal of bromate formed in ozonated groundwater were developed [9]. According to statistical performance values, the best result was obtained with the artificial neural network model. In another modelling study, artificial neural networks to evaluate trihalomethane, haloacetic acid and total organic halides resulting from chlorination [10]. In addition to these studies, bromide removal experiments were carried out under different operating conditions in an adsorption column system using pure and 3 different modified granular activated carbon and experimental results were modeled with an artificial neural network [11]. In modeling studies, particle size, activated carbon amount, column height, column diameter and bromide removal, which was determined as the initial concentration input variable, were defined as output. Model performance was determined by correlation coefficient, mean absolute percentage error and root mean square error. While R, RMSE and MAPE values were calculated as 0.993, 2.66 and 3.65%, respectively, in the training phase, R, RMSE and MAPE values were calculated as 0.988, 3.47 and 5.19%, respectively.

In this study, the adsorption column with technical and modified activated carbons was used for the removal of bromate ion formed as a result of ozonation in drinking water. Within the scope of experimental studies, the effects of particle size, activated carbon amount, column height and diameter, volumetric flow rate and initial concentration on bromate removal were investigated. After the experimental data was taken, the model was developed to predict bromate removal with least squares support vector machine (LS-SVM) to predict bromate removal. During the development of the model, 48 data were used, 34 of which (70%) were educational data, and 14 were randomly selected as test data. As activation function, radial based kernel function (Radial Basis Function-Kernel, RBF-Kernel) was used and γ and σ^2 values, which are the parameters of the model, were determined as 415 and 3.956, respectively. In this modeling study where bromate removal is predicted; particle size, amount of activated carbon, column height and diameter, volumetric flow rate and initial concentration value are defined as the input variable of the model. To determine the success of the model, correlation coefficient, mean absolute percentage error and root me an square error statistical performance values were calculated. According to statistical performance values, the least squares support vector machines model has yielded very successful results in the prediction of bromate removal in drinking water. On the other hand, the results of this study were compared with the artificial neural network modeling (ANN) study [11], which was previously done with the same examples and data set, and it was determined that the least squares support vector machines model produced more successful results.

2. MATERIALS AND METHODS

2.1. Experimental Studies

Technical and modified activated carbon samples were prepared for the removal of bromate ion formed by disinfection of drinking water with ozone. Bromate removal was carried out in the vertical adsorption column given in Figure 1.

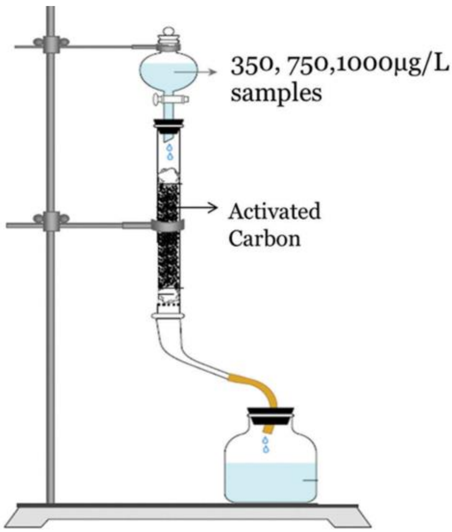

Figure 1. Granular activated carbon adsorption column used in bromate ion removal [11]

Experimental methods for preparing pure (technical) and modified activated carbons in granular form are presented below. Within the scope of the modification studies, hydrochloric acid (HCl), sodium hydroxide (NaOH) and ammonia (NH_3) were used. Activated carbons were modified using 1 M HCl, 0.1 M NaOH and 15% NH_3 solutions.

2.1.1. Preparation of Pure Activated Carbon

Granular activated carbon used in experimental studies is taken from the market. However, due to the non-homogeneous particle size of the activated carbon, the sieving process was carried out. Activated carbon samples, selected between 0.4-0.8 mm and 1.4-1.7 mm, were washed with distilled water for use in experimental studies. These samples were dried in the oven at 105^{o}C for 24 hours. Samples that the particle size 1.4-1.7 mm was used in the modification studies.

2.1.2. Preparation of HCl Modified Active Carbons

40 g ± 1 g of pure activated carbon samples prepared in the above step were added in 400 ml and 1.0 M HCl solution and kept in the shaker for 24 hours. Modified activated carbon samples were dried in the oven at 105^{o}C for 24 hours after washing with distilled water.

2.1.3. Preparation of NaOH Modified Active Carbons

During the preparation phase of NaOH modified activated carbon samples, 400 mL of 0.1 M NaOH solution was added to 40 g ± 1 g of pure activated carbon sample and kept in a shaker for 24 hours. Modified activated carbon samples were dried in the oven at 105^{o}C for 24 hours after washing with distilled water.

2.1.4. Preparation of NH_3 Modified Active Carbons

During the preparation phase of activated carbon samples modified with NH_3, 200 mL of 15% NH_3 solution was added over 40 g ± 1 g and kept in the shaker for 24 hours. The modified activated carbon samples were dried for 24 hours in an oven at 105^{o}C after washing with distilled water.

2.1.5. Preparation of Synthetic Water Samples

In this study, bromide ion solutions in three different concentrations (350 μg / L, 750 μg / L and 1000 μg / L) were prepared. Particle size, modification type of activated carbon, diameter and height of adsorption column and flow rate parameters were investigated on bromate removal. In this context, 1, 2 and 3 cm diameter 2, 5 and 10 cm high columns were used. In studies examining particle size, 0.4-0.8 mm and 1.4-1.7 mm diameter particles were used, while flow rates of 10, 25 and 50 ml / min were chosen. The amount of bromate in the samples was analyzed by high performance liquid chromatography (HPLC) (Thermo ICS-3000).

2.2. Modelling Study

2.2.1. Least Squares Support Vector Machine (LS-SVM)

Support Vector Machine (SVM) is known as kernel based statistical learning methodology and it is used for solving problems of nonlinear classification, estimation and pattern recognition. Support vector machines solve generally the convex optimization problems. In the optimization step, the least squares support vector machines method is used to alleviate the computational load caused by nonlinearity [12]. The schematic representation of LS-SVM algorithm is given in Figure 2.

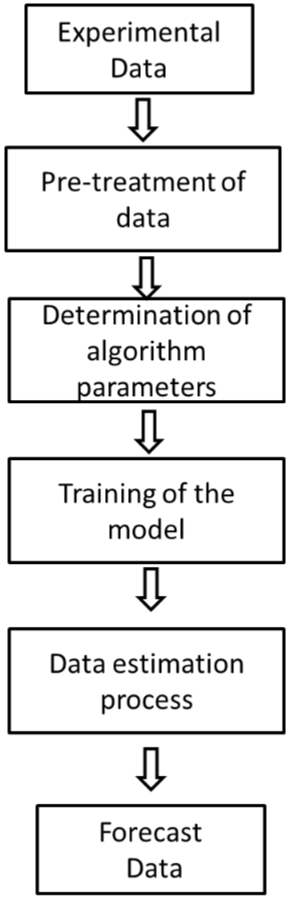

Figure 2. LS-SVM algorithm flow diagram

The equations for the least squares support vector machine algorithm are given below [13].

$\{(x_1, y_1), .., (x_k, y_k)\}$ training set and the regression model can be written as follows using the nonlinear mapping function

$$Y=w^T\Phi(x)+b \quad w \in R_N \quad b \in R \quad \Phi \in R_N \rightarrow R_M \quad M \rightarrow \infty \tag{1}$$

In this equation, w is the weight vector and b is the bias value. When the least squares support vector is used as an approximate function, the optimization problem of LS-SVM takes the following form:

$$\min_{w,e} J(w,e) = \frac{1}{2} W^T w + \frac{\gamma}{2} \sum_{k=1}^{N} e_k^2 \tag{2}$$

Constraint of this problem is given in Equation 3.

$$y_k = w^T \Phi(x_K) + b + e_k \quad k = 1, 2........N \tag{3}$$

The parameter given in Equation 2 is the editing parameter (γ) and provides the balance between model complexity and training error. On the other hand, it is the error value based on the difference between the additional real value and the calculated value. To solve the optimization problem with constraint function, Lagrange function is defined (Equation 4)

$$L(w,b,e,\alpha) = J(w,e) - \sum_{k=1}^{N} \alpha_k \{w^T \Phi(x_k) + b + e_k - y_k\} \quad (4)$$

α_k is the Lagrange multiplier given in Equation 4 and is known as the support vector. For the solution of equation 4, it is equal to zero among the partial derivatives of the equation according to a parameter. These equations are found collectively in Equation 5.

$$\frac{\partial L}{\partial w} = 0 \Rightarrow w = \sum_{k=1}^{N} \alpha_k \Phi(x_k)$$
$$\frac{\partial L}{\partial b} = 0 \Rightarrow \sum_{k=1}^{N} \alpha_k = 0 \quad (5)$$
$$\frac{\partial L}{\partial e_k} = 0 \Rightarrow \alpha_k = \gamma e_k$$
$$\frac{\partial L}{\partial e_k} = w^T \Phi(x_k) + b + e_k - y_k = 0 \quad k = 1.........N$$

From the equations obtained, the linear form equation is obtained as in Equation 6. [12, 13]

$$\begin{bmatrix} 0 & \vec{1}^T \\ \vec{1} & Z + \gamma^{-1} I \end{bmatrix} \begin{bmatrix} b \\ \alpha \end{bmatrix} = [0] \quad (6)$$

Herein; $y=[y_1,\ldots y_N]$, $\vec{1} = [1,\ldots,1]$ $\alpha = [\alpha_1 \ldots \alpha_N]$ $Z = \{Z_{kj} | k, j = 1, \ldots, N\}$ (7)

$$Z_{kj} = F(x_k)^T F(x_j) = K(x_k, x_j) \quad k, j = 1, \ldots, N$$

K (x_k, x_j) shown in Equation 7 is defined as the kernel function. So the least squares support vector machines are given in Equation 8.

$$y(x) = \sum_{k=1}^{N} \alpha_k K(x, x_k) + b \quad (8)$$

3. RESULT AND DISCUSSION

This study presents experimental and modeling studies on bromate removal from drinking water. The radial basis kernel function was selected as the activation function in the algorithm. Algorithm parameters that γ and σ^2 values determined 415 and 3.956 as respectively. Statistical performance values are presented in Table 1. The results of this study were compared with a study carried out in our group previously [11]. According to the results, LS-SVM algorithm prediction was very successful and better than the ANN algorithm developed in a previous study.

Table 1. Statistical performance value of the models

Model	Training Data			Test Data			
	R	MAPE%	RMSE	R	MAPE%	RMSE	
LS-SVM	0.996	2.59	2.14	0.994	3.21	2.51	This study
ANN	0.993	3.65	2.66	0.988	5.19	3.47	[11]

The compatibility of the model results and experimental data in test and training results were presented in Figure 3 and Figure 4.

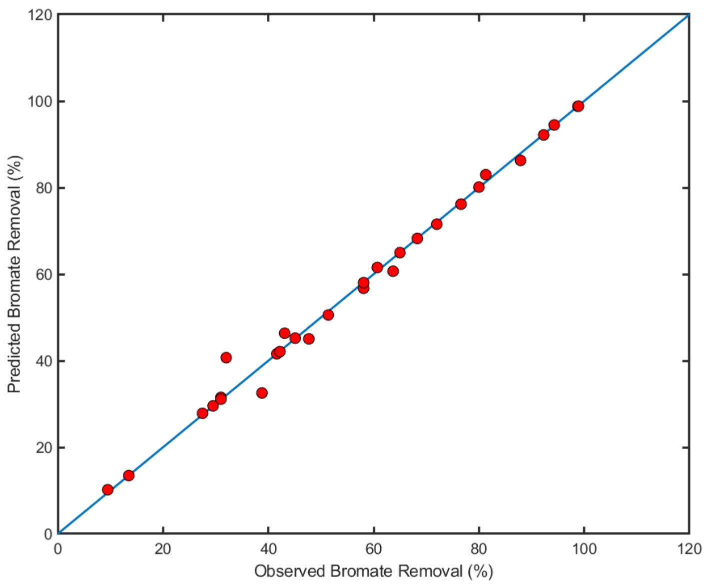

Figure 3. Experimental data- model predictions result compatibility for training data

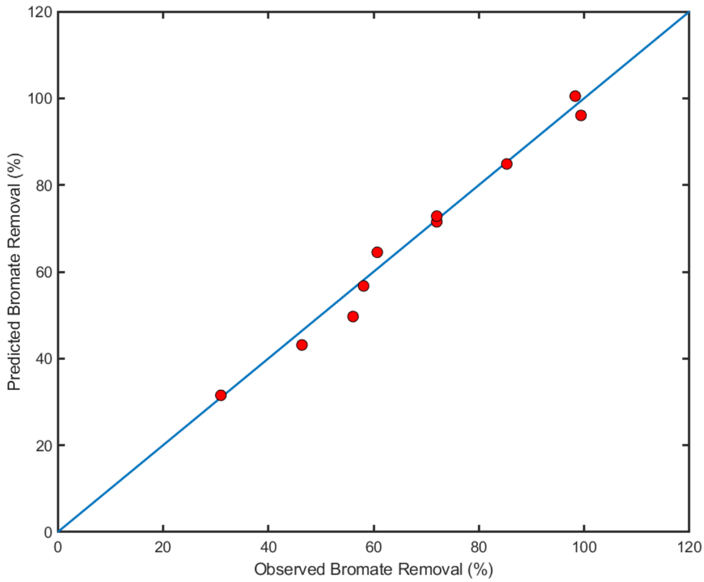

Figure 4. Experimental data-model predictions result compatibility for test data

4. CONCLUSION

In recent years, rapid reduction and pollution of water resources due to due to unconscious use, some measures have become necessary. Disinfection of drinking water, which is very important for living life, is inevitable. However, by-products formed as a result of many disinfection processes must be removal. In this study, activated carbon in different forms were used to remove bromate in synthetic samples in different concentrations.

After obtaining experimental data in the laboratory, the bromate prediction model was developed by using LS-SVM which one of the artificial intelligence methods.

The innovative part of the study is that artificial intelligence/machine learning methods, which are limited in the literature, have been successfully applied to drinking water data. The results of this study were compared with ANN, another machine learning method previously done in our research group, and it was concluded that the results obtained with LS-SVM were better. According to the results given in Table 1, the least squares support vector machines model produced more successful results compared to the artificial neural network model. As a result; The least squares support vector machines method can be used to predict bromate removal from drinking water.

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