I.A.U. Karaj Branch

Journal of Applied Chemical Research, 10, 2, 25-37 (2016)

Journal of Applied Chemical Research

www.jacr.kiau.ac.ir

Application of Response Surface Methodology and Artificial Neural Network for Analysis of *p*-chlorophenol Biosorption by Dried Activated Sludge

Vahid Reza Fanaie[1], Mohsen Karrabi[1*], Mohammad Mehdi Amin[2], Bahar Shahnavaz[3] Ali Fatehizadeh[2]

[1]Civil Engineering Department, Faculty of Engineering, Ferdowsi University of Mashhad, Mashhad, Iran

[2]Environmental Health Engineering Department, Isfahan University of Medical Science, Isfahan, Iran

[3]Department of Biology, Faculty of Science, Ferdowsi University of Mashhad, Mashhad, Iran

(Received 17 Jan. 2016; Final version received 18 Mar. 2016)

Abstract

Phenolic compounds are considered as priority pollutants because of their high toxicity at low concentration. In the present study, the sorption of *p*-chlorophenol (*p*-CP) by dried activated sludge was investigated. Activated sludge was collected as slurry from the sludge return line of a municipal wastewater treatment plant. Sorption experiments were carried out in batch mode. In order to investigate the effect of operating parameters on the removal efficiency of *p*-CP, four independent variables, including pH, initial concentration of *p*-CP, contact time and adsorbent dosage were studied. Artificial neural network (ANN) and response surface methodology (RSM) were developed for modeling of biosorption process. Results indicated that, Dried activated sludge can efficiently remove *p*-chlorophenol from aqueous solutions. The RSM method suggested that pH is the most significant parameter for biosorption process. Finally, RSM technique gave a function and neural network gave a structure for prediction. Neural network have a higher degree of accuracy and ANN predicted outputs were closer to the actual outputs of experiments in comparison with RSM technique.

Keywords: *Biosorption, p-chlorophenol, Sludge, Neural Network, RSM.*

Introduction

Phenolic compounds are regarded as priority pollutants because of their high toxicity even at low concentration [1, 2]. Chlorophenols give an undesirable taste and odor to drinking water and can exert negative effects on

***Corresponding author:** Dr. Mohsen Karrabi, Civil Engineering Department, Faculty of Engineering, Ferdowsi University of Mashhad, Mashhad, Iran. E-mail: karrabi@um.ac.ir, Tel.: +98 5138805154, Fax: +98 5138806053.*

different biological processes [3]. Most of these compounds are known or suspected to be a health hazard. The main pollution sources containing chlorophenols are the wastewaters from pesticide, paint, solvent, pharmaceutics, wood, pulp and paper industries [3, 4].

According to the literature, various processes have been employed for the removal of chlorophenols from aqueous solution, such as activated carbon adsorption, chemical oxidation, aerobic/anaerobic biological degradation, coagulation, solvent extraction and liquid membrane permeation [5, 6]. However, due to the disadvantages such as relatively high cost and tedious procedures for its preparation and regeneration of activated carbon, there is a growing interest in the use of low cost and unconventional adsorbents [6, 7]. Among these biosorbent, activated sludge is a well-known biomass used for the removal of phenolic compounds. In addition, some fungal mycelia and bacterial biomass have also been utilized to remove phenolic compounds through adsorption [8, 9]. The accumulation of chemicals on the surface of the cell wall of microorganisms has been defined as biosorption. Since the physicochemical mechanisms in the biosorption are complex, no simple theory of adsorption could adequately describe experimental results.

For a mono-component system Langmuir and Freundlich isotherms and pseudo first and second order models have been the most common adsorption models used for equilibrium and kinetic studies. However, these models may find to be deficient in describing the connection between the factors and evaluating their impact on the biosorption process. To overcome this problem multivariate statistical techniques have been used. Response surface methodology (RSM) and artificial neural network (ANN) are among the most popular used methods in research on biosorption literature [10, 11]. RSM is a collection of statistical and mathematical tools used to optimize the response controlled by several independent variables. Classically, response is optimized by changing one parameter at a time and keeping other parameters constant. By taking into account various independent parameters, optimization is achieved through RSM [12]. Artificial neural networks (ANN), have been used for representing non-linear relationships between variables. The ability of an ANN to learn and generalize the behavior of any complex and non-linear process makes it a powerful modeling tool [11, 13]. The neural network can be trained to perform a particular function by adjusting the values of connections (weights) between elements. Prediction of biosorption of heavy metals from aqueous solution has been attempted in the past by many researchers using ANN to a reasonably good degree of success [14, 15]. In the present study, the objectives were (*i*) to investigate the sorption of p-chlorophenol (*p*-

CP) by dried activated sludge (*ii*) to develop RSM and ANN models for biosorption process (*iii*) to compare both RSM and ANN with each other

Experimental

Chemicals

p-chlorophenol (>99% purity) was purchased from Merck Ltd., Germany, and was used without further purification. All other inorganic chemicals were of analytical grade and were purchased from Merck., Germany. The stock solution of 1000 mg/L was prepared by dissolving p-CP (M=128.56 g/mol) in deionized water. The p-CP concentrations of prepared solutions varied between 5 and 30 mg/l in the sorption experiments and all working concentrations were obtained by diluting the stock solution with deionized water. The pH value of the solution in this study (2.0–11.0) was adjusted to the required value by adding 1M NaOH or 1M HCl solutions [16]. All solutions were stored in the dark at 4 oC prior to use.

Preparation of Biosorbent

Activated sludge was collected as slurry from the sludge return line of a municipal wastewater treatment plant in Isfahan, Iran. Activated sludge was dried at 105 °C for 24 h to reach a constant weight and then grounded and sieved to obtain particle size below 0.35 mm. Thereafter, dried sludge was protonated by adding 50 g of the raw sludge biomass into 1L of HCL solution (0.1 mol/L) and then stirring the mixture at 250 rpm for 30 min at 25±1 °C. Finally, the acid treated biomass was washed with deionized water several times to remove excess hydrogen ions and again dried at 105 °C for 24 h [17].

Experimental Procedures

Sorption experiments were carried out in batch mode. The 250-mL conical flasks were used for mixing the desired amount of the sludge biomass with 100 ml solution of known p-CP concentration. The effect of initial pH values, initial p-CP and biomass concentration as well as contact time on p-CP removal was studied as tabulated in Table 1. Flasks were agitated on a shaker at 250 rpm at room temperature 25±1 °C. After the adsorption period, the adsorbents were separated by filter papers. The residual concentration of p-CP was analyzed by measuring the absorbance of the red complex of p-CP solutions by a spectrophotometer (Milton Roy). The amount of adsorption at equilibrium, q (mg/g) was obtained as follows:

$$q = \frac{[(C_0 - C_e).V]}{m} \qquad (1)$$

where C_0 and C_e are the initial and equilibrium concentration (mg/L); V is the volume of the solution (L); and m is the weight of the dry biomass used (g).

Table 1. Experimental parameters for p-CP removal process.

Tests	Biomass con. (g/L)	Initial p-CP con. (mg/L)	pH	Time (min)
Biomass dosage	5-30	5-30	4	240
Initial concentration	5-30	5-30	4	240
pH	5-10	5-10	2-11	90
Contact time	20	20-40	4	5-360

Response surface methodology

The RSM method is based on the fit of mathematical models (linear, square, polynomial functions and others) to the experimental results generated from the designed experiment and the verification of the model obtained by means of statistical techniques. In order to investigate the effect of operating parameters on the removal efficiency of p-CP, four independent variables were chosen: pH, initial p-CP concentration, time, adsorbent dosage. The next crucial step is design of experiments with the selection of points where the response should be estimated. Several design methods have been applied for biosorption experiments, but the central composite design (CCD) is widely used form of RSM [18]. This method is suitable for fitting a quadratic surface and it helps to optimize significant parameters with minimum number of experiments, as well as to analyze the interaction between the parameters. The total number of experiments by operating CCD of RSM in design expert software (Version 7.0.0, Stat. Ease. Inc, United States) was 30. Removal efficiency was selected as the observed response which was correlated with the coded values of the variables by means of the following general second-order polynomial equation [11, 13]:

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_{i=1}^{k} \sum_{i \neq j=1}^{k} \beta_{ij} X_i X_j \qquad (2)$$

where y is the observed response, β_0 is a constant coefficient, β_i, β_{ii} and βij are the coefficients for the linear, quadratic and interaction effects, respectively. Xi and X_j represent the coded independent variables; k is the number of the independent variables (4 in this case). The least squares methods were used to verify the results and individual linear, quadratic and interaction terms were determined by the analysis of variance (ANOVA) with Stat-Ease V7 software.

Artificial neural network

In the present work, as it is shown in Figure 1 a typical three layer feed-forward neural network consists of input, output and a single hidden layer with a tangent sigmoid transfer function (tansig) at hidden layer and a linear transfer function (purlin) at output layer was used for modelling of the p-CP adsorption capacity.

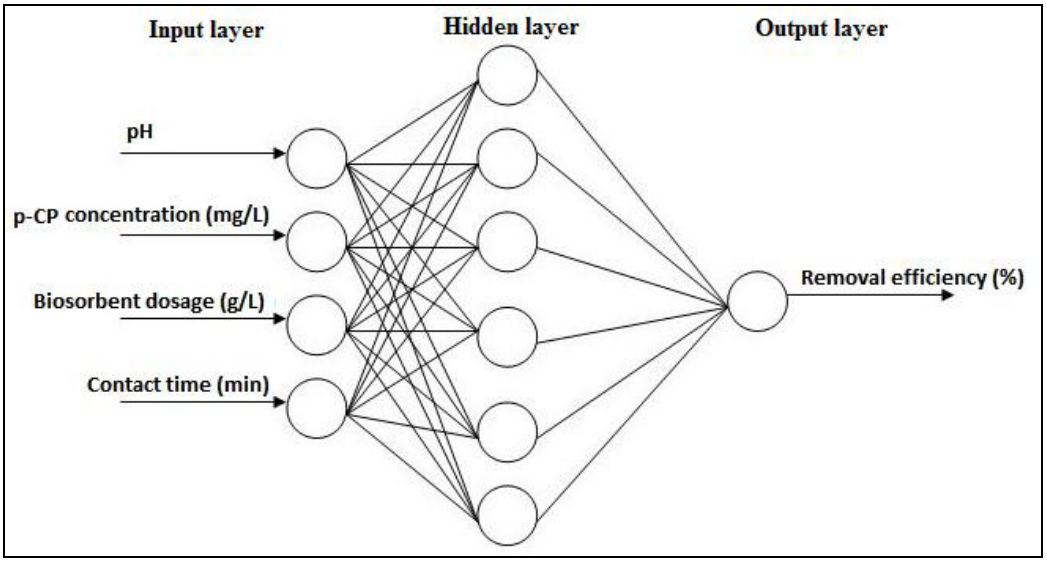


Figure 1. Neural network architect for the removal of p-CP.

The input layer consists of four experimental parameters including the contact time (hour), initial p-CP concentration (mg/L), biosorbent dosage (g/L) and pH. The output layer was removal percentage (%). To determine the optimum number of nodes in the hidden layer 1-20 neurons were used. All data derived from experiments (X_i) were scaled in 0.1-0.9 range (A_i) using Eq. 3, and then divided into training, validation and test sets with a ratio of 70%, 15% and 15%, respectively.

$$A_i = 0.8\left(\frac{X_i - \min(X_i)}{\max(X_i) - \min(X_i)}\right) + 0.1 \qquad (3)$$

where $\min(X_i)$ and $\max(X_i)$ are the extreme values of the input variables (X_i) and Ai is the normalized value. The performance of the network was evaluated by the mean squared error (MSE) and the coefficient of determination (R^2) which can be defined as follows [19, 20]:

$$MSE = \frac{1}{N}\sum_{i=1}^{N}(|y_{prd,i} - y_{exp,i}|)^2 \qquad (4)$$

$$R^2 = 1 - \frac{\sum_{i=1}^{N}(y_{prd,i} - y_{exp,i})}{\sum_{i=1}^{N}(y_{prd,i} - y_m)} \qquad (5)$$

where $y_{prd,i}$ was the predicted value by ANN model, $y_{exp,i}$ was the experimental value, was the number of data and y_m was the average of experimental values.

Results

SEM and FT-IR

SEM and FT-IR techniques were used to investigate the morphological and functional groups of biosorbent surface. From the Figure 2, it can be implied that biosorbent surface has a high porosity texture. The FT-IR analysis is important to specify different functional groups onto the biosorbent which are responsible for biosorption of *p*-CP.

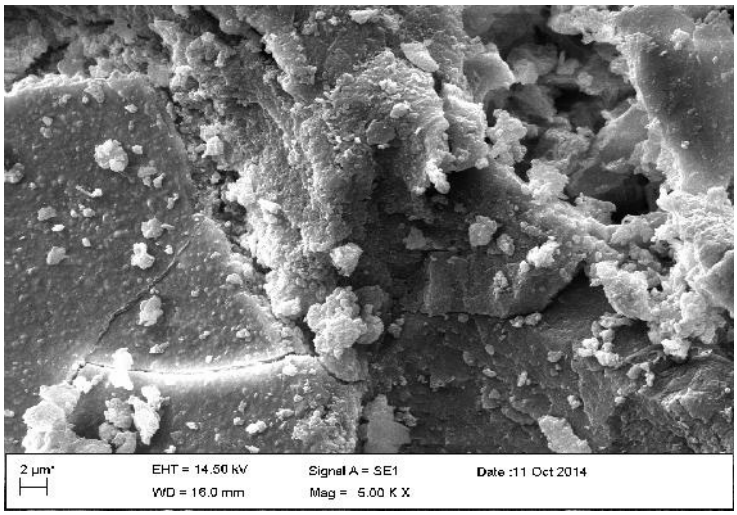


Figure 2. SEM micrograph of DAS surface.

Figure 3 shows the FT-IR spectra of DAS before and after adsorption of *p*-CP. The bands appearing at about 469 cm^{-1} , 471 cm^{-1} and 467 cm^{-1} that are seen in all of the spectra, are related to bending vibrations of O—P—O in phosphate groups. The peaks located at 533 cm-1, 874 cm^{-1} and 796 cm^{-1} assigned to C—Cl stretching vibrations of aromatic ring are the great evidence for the absorption of p-chlorophenol on the surface of the sludge. The absorptions around 1032 cm^{-1}, 1037 cm^{-1} are due to stretching vibrations of the P—O bond. The peaks at 1652 cm^{-1}, 1639 cm^{-1}, 1428 cm^{-1} and 1450 cm^{-1} are attributed to C—C bonds vibration of aromatic rings. The increasing intensity of these peaks after the absorption confirms the existence of the *p*-CP.

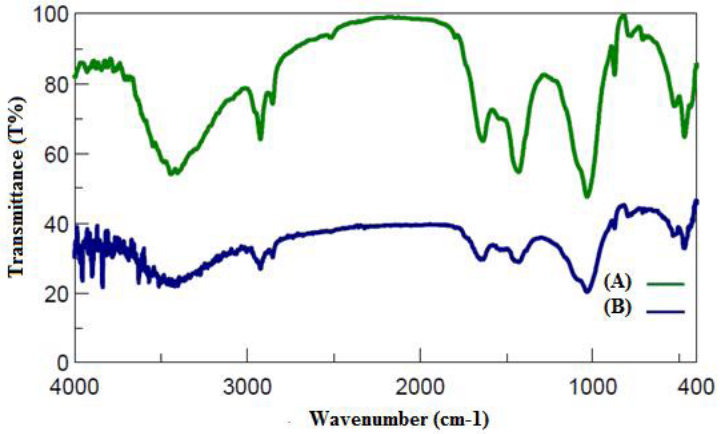


Figure 3. FT-IR spectra of DAS **(A)** before adsorption **(B)** after adsorption.

The absorption peaks at 2854 cm^{-1} and 2925 cm^{-1} are related to stretching vibrations of aliphatic C—H bonds. The small peaks at 3277 cm^{-1}, 3285 cm^{-1}, 3374 cm^{-1}, 3345 cm^{-1} are attributed to the vibrations of aromatic C—H bonds. The absorptions located at 3448 cm^{-1}, 3512 cm^{-1}, 3565 cm^{-1}, 3548 cm^{-1} and 3610 cm^{-1} are assigned to O—H bonds of sludge

and aromatic rings.

Response surface method

The coded levels of variables as the minimum (-1), zero (0) and maximum (+1) levels of the factors were shown in Table 2. All experiments were carried out and the results obtained according to design matrix were shown in Table 3. The final equation in terms of coded factors for the removal approximation of p-CP is presented below:

$$Removal\ (\%) = +72.89 - 19.80\,A - 6.54\,B + 11.31\,C + 9.64\,D + 3.33\,AB - 0.95\,AC - 6.15\,AD - 0.17BC - 3.06BD + 3.11CD - 6.90A^2 - 11.43B^2 - 10.63C^2 - 6.93D^2 \quad (6)$$

Table 2. Independent variables and their coded values.

Factor	Name	Units	minimum actual	maximum actual	zero	minimum coded	maximum coded	zero coded
A	pH	-	2	11	6.5	-1	+1	0
B	Int.con	mg/l	5	40	22.5	-1	+1	0
C	Dosage	g/l	5	30	17.5	-1	+1	0
D	Contact time	min	5	360	182.5	-1	+1	0

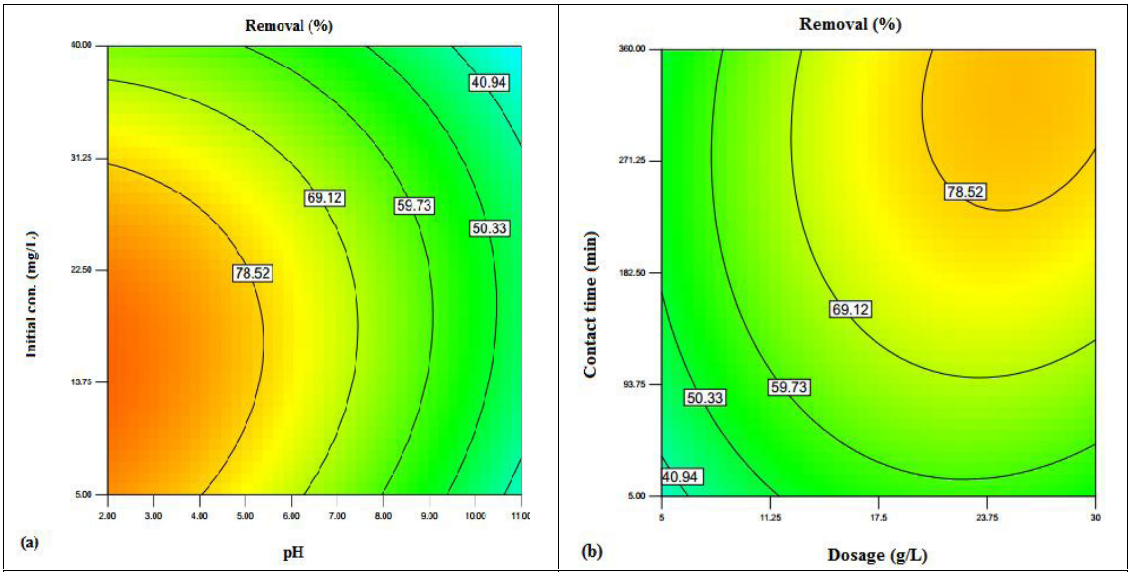
Table 3. Experimental data for CCD design.

Run	Actual and coded levels of variables				Removal (%)
	pH	Int.con (mg/L)	Dosage (g/L)	Contact time (min)	
1	2 (-1)	5 (-1)	5 (-1)	360 (+1)	75.4
2	6.5 (0)	22.5 (0)	17.5 (0)	182.5 (0)	77.3
3	2 (-1)	5 (-1)	30 (+1)	360 (+1)	96.5
4	6.5 (0)	22.5 (0)	17.5 (0)	5 (-1)	41.2
5	11 (+1)	5 (-1)	5 (-1)	360 (+1)	14.3
6	11 (+1)	40 (+1)	5 (-1)	5 (-1)	10
7	2 (-1)	22.5 (0)	17.5 (0)	182.5 (0)	88.65
8	6.5 (0)	22.5 (0)	17.5 (0)	182.5 (0)	75.6
9	6.5 (0)	22.5 (0)	17.5 (0)	182.5 (0)	76.1
10	6.5 (0)	5 (-1)	17.5 (0)	182.5 (0)	62.3
11	11 (+1)	5 (-1)	5 (-1)	5 (-1)	11.1
12	11 (+1)	40 (+1)	30 (+1)	5 (-1)	18.88
13	11 (+1)	40 (+1)	30 (+1)	182.5 (+1)	22.4
14	2 (-1)	40 (+1)	5 (-1)	5 (-1)	32.8
15	6.5 (0)	22.5 (0)	30 (+1)	182.5 (0)	93.2
16	6.5 (0)	22.5 (0)	17.5 (0)	182.5 (0)	77.3
17	11 (+1)	5 (-1)	30 (+1)	360 (+1)	36.7
18	6.5 (0)	22.5 (0)	17.5 (0)	360 (+1)	80.2
19	6.5 (0)	22.5 (0)	17.5 (0)	182.5 (0)	77.4
20	2 (-1)	5 (-1)	30 (+1)	5 (-1)	50.8
21	2 (-1)	40 (+1)	30 (+1)	360 (+1)	73.9
22	2 (-1)	40 (+1)	30 (+1)	5 (-1)	41.2
23	6.5 (0)	22.5 (0)	5 (-1)	182.5 (0)	20.8
24	11 (+1)	5 (-1)	30 (+1)	5 (-1)	26.5
25	11 (+1)	22.5 (0)	17.5 (0)	182.5 (0)	32.8
26	11 (+1)	40 (+1)	5 (-1)	360 (+1)	11.14
27	2 (-1)	5 (-1)	5 (-1)	5 (-1)	42.8
28	6.5 (0)	40 (+1)	17.5 (0)	182.5 (0)	50.1
29	6.5 (0)	22.5 (0)	17.5 (0)	182.5(0)	77.9
30	2 (-1)	40 (+1)	5 (-1)	360 (+1)	38.2

Analysis of variance (ANOVA) was applied to examine the model accuracy. The parameter coefficients, the associated standard errors and the effect of each term in Eq. 6 are presented in Table 4. In this case, all first order values (A, B, C, and D) are significant model terms. The value of the determination coefficient (R^2=0.89) indicated that, 11% of the total variation is not explained by the regression model. The high value of the adjusted determination coefficient (R_{adj}^2=0.83) implicates to the significance of the model. Figure 4 (a, b, c and d) shows the combined effect of pH and initial concentration, dosage and contact time, pH and dosage, initial concentration and contact time. It is clear from the figures that with increasing dosage and contact time, removal capacity will be increased and also pH degree ranges between 2 and 4 improve the removal of p-CP by DAS.

Table 4. Statistical analysis and significance components in the quadratic model.

Term	Coefficients	Standard errors	P-values
A	-19.80	3.00	≤ 0.0001
B	-6.54	3.00	0.0454
C	11.31	3.00	0.0019
D	9.64	3.00	0.0058
AB	3.33	3.18	0.3122
AC	-0.95	3.18	0.7684
AD	-6.15	3.18	0.0724
BC	-0.7	3.18	0.959
BD	-3.06	3.18	0.3515
CD	+3.11	3.18	0.3425
A^2	-6.90	7.90	0.3963
B^2	-11.43	7.90	0.1688
C^2	-10.63	7.90	0.1988
D^2	-6.93	7.90	0.3947
Intercept	-	3.95	-
R^2 = 0.89		R^2_{adj} = 0.83	



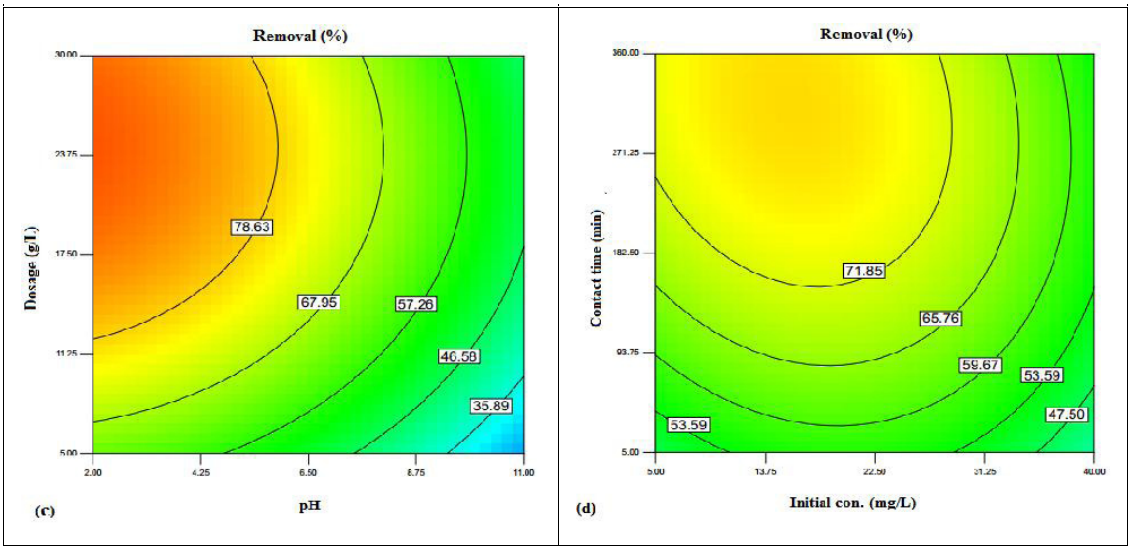


Figure 4. Effect of **(a)** pH and initial concentration **(b)** dosage and contact time **(c)** pH and dosage **(d)** initial concentration and contact time on adsorption capacity of p-CP by DAS.

Neural network

Specifying the number of hidden layer neurons in design of neural network is a very important step. Unfortunately, there is no specific method for determining the optimal number of hidden layer neurons and in most of the cases, trial and error approach have been used by researchers to select the number of neurons. In the present study, different number of neurons in the range of 1-20 was adopted in the hidden layer. According to Figure 5 the optimum number of neurons in the hidden layer is equal to 6 as the best case with the minimum value of MSE (8.41×10^{-4}) and high value of R^2= 0.98. Therefore a three layer feed forward neural network (4:6:1) was used for modeling of adsorption process. As it is shown in Figure 6, a comparison between actual and predicted data for test and validation data give a clearer insight to the neural network performance. It has been shown in Figure 6 that the differences between experimental and predicted data are negligible and can be ignored.

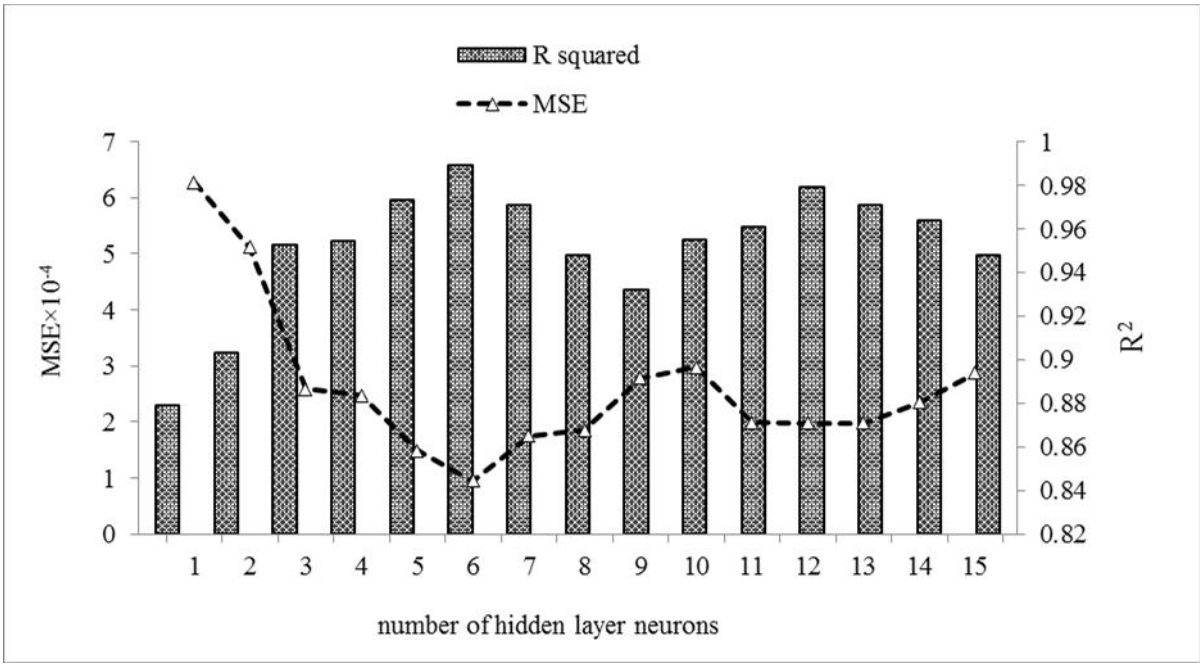


Figure 5. Effect of number of hidden layer neurons on the performance of neural network.

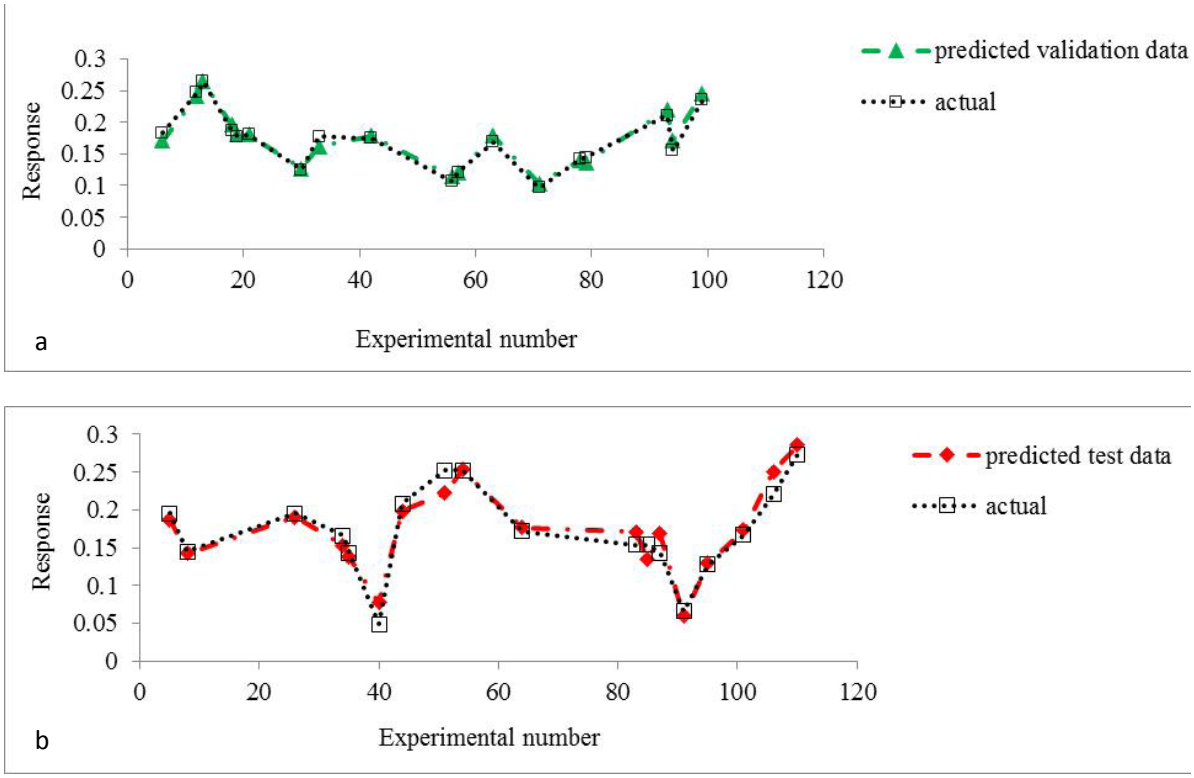


Figure 6. (a) Comparison between actual and predicted validation data. **(b)** Comparison between actual and predicted test data.

Discussion

RSM technique has some advantages in comparison with ANN. For example, RSM method gives a regression equation for prediction and showing the effect of experimental parameters on the response. However, this method, assumes linear, quadratic and cubic form of correlation of any data set, but ANN can capture any form of non-linearity and doesn't need standard experimental design to build up model [11, 13]. In this study, the performance of the models, which was measured by determination coefficient (R^2), indicated that, ANN method has better capability for prediction of removal capacity of DAS in comparison with RSM. Deniz bingol et al. evaluated the capability of RSM and ANN for prediction of heavy metals biosorption process. They concluded that the ANN has better performance for biosorption predictions in comparison with RSM [13]. Rahimpour et al. used light expended clay aggregate (LECA) for adsorption of Cu^{2+} and employed ANN and RSM for modeling of adsorption process. Results indicated that the determination coefficient for both models are close to each other and both models almost have the same capability for process prediction [21]. Coruh et al. used NARX neural network model for adsorption of zinc ion by almond shell [22]. The result showed that removal efficiencies produced by experiments and ANN model are close to each other and in an acceptable error limit. From the Figure 4, it is apparent that the removal of p-CP increase rapidly with an increase in the dosage of adsorbent due to greater availability of binding sites of the biosorbent. The initial pH of adsorption medium is one of the most important parameters affecting the adsorption process. pH primarily affects the surface properties of biosorbent and the degree of ionization of phenolic compounds. A wide range of pH values (2-11) were applied in this study to examine the effect of pH on sorption capacity. The overall surface charge on the cells became positive when pH is lower than the isoelectric point of biomass. The isoelectric point of activated sludge would be usually between pH 1 and 3 and this situation led to the interactions between the aromatic ring of p-CP activated by the OH- and Cl- and the groups of biosorbent surface. As the pH increased, the overall surface charge on the cells became negative and the biosorption between negatively charged phenolic compounds and binding sites of the biomass surface decrease. The degree of ionization is another determining factor. When pH is not more than one unit above pKa values of p-CP (9.41), Non-dissociated forms activated by the OH- and Cl- dominated the overall sorption of chlorinated phenols on organic sorbent. When pH is greater than pKa values of p-CP, negatively charged ionized forms dominate in the solution.

Conclusion

Dried activated sludge was efficient as a biosorbent for the removal of *p*-chlorophenol from aqueous solutions. The *p*-CP biosorbent interactions were confirmed by FT-IR and heterogeneous, smooth and porous structure were observed by SEM technique. The present work suggests that, ANN predicted results were close to experimental values. The average mean square error was 0.95×10^{-4} which was sufficient to have an error within ± 1.0%. A high degree of correlation (R^2=0.98) between actual and predicted sorption efficiency was observed for data set.

The RSM method gave a function for prediction of biosorption process and also this method suggested that pH is the most significant parameter. The value of the determination coefficient was 0.89 (R^2=0.89). RSM graphs indicated that increasing in absorbent dosage and contact time lead to increase the removal efficiency, whereas by increasing initial concentration of *p*-CP the removal efficiency was reduced. pH in the range of 2-4 was the optimum for higher removal efficiency. Finally, ANN technique has higher value of the determination coefficient in comparison with RSM method. Therefore ANN technique can predict responses with a high degree of accuracy.

Acknowledgement

The authors would like to thank the Environmental Research Center at Isfahan University of Medical Sciences. This work was supported by Ferdowsi University of Mashhad grants Nº 28749/3.

References

[1] Z. Aksu, *Process. Biochem*., 40, 997 (2005)

[2] A. Denizli, N. Cihangir, N. Tüzmen, G. Alsancak, *Bioresour. Technol*., 96, 59 (2005)

[3] S.K. Nadavala, K. Swayampakula, V.M. Boddu, K. Abburi, *J. Hazard. Mater.,* 162, 482 (2009)

[4] R. Gao, J. Wang, *J. Hazard. Mater.,* 145, 398 (2007)

[5] K.J. Kennedy, J. Lu, W.W. Mohn, *Water. Res*., 26, 1085 (1992)

[6] W. Wang, W. Wang, X. Zhang, D. Wang, *Water. Res*., 36, 551 (2002)

[7] S.H. Lin, R.S. Juang, *J. Environ. Manage.,* 90, 1336 (2009)

[8] V.M. Monsalvo, A.F. Mohedano, J.J. Rodriguez., *Chem. Eng. Res*., 90, 1807 (2012)

[9] K.Vijayaraghavan, Y.S. Yun, Biotechnol. Adv., 26, 266 (2008)

[10] A.R. Khataee, M.B. Kasiri, *J. Mol. Catal. A. Chem.*, 331, 86 (2010)

[11] A.Witek-Krowiak, K. Chojnacka, D. Podstawczyk, A. Dawiec, K. Pokomeda, *Bioresour. Technol*., 160, 150 (2014)

[12] D. Gusain, F. Bux, Y.C. Sharma, *J. Mol. Liq.*, 197, 131 (2014)

[13] D. Bingöl, M. Hercan, S. Elevli, E. Kılıç, *Bioresour. Technol*., 112, 111 (2012)

[14] A. Çelekli, H. Bozkurt, F. Geyik, *Bioresour. Technol*., 129, 396 (2013)

[15] A. Hassani, F. Vafaei, S. Karaca, A. R. Khataee, *J. Ind. Eng. Chem*., 20, 2615 (2014)

[16] J. Wu, HQ. Yu, *J. Hazard. Mater.*, 137, 498 (2006)

[17] M. L. Paul, J. Samuel, N. Chandrasekaran, A. Mukherjee, *Chem. Eng. J.,* 187, 104 (2012)

[18] A. Boubakri, A. Hafiane, S. A. T. Bouguecha, *J. Ind. Eng. Chem.,* 20, 3163 (2014)

[19] M. F. Ahmad, S. Haydar, A. A. Bhatti, A. J. Bari, *Biochem. Eng. J*., 84, 83 (2014)

[20] A. K. Giri, R. K. Patel, S. S. Mahapatra, *Chem. Eng. J.,* 178, 15 (2011)

[21] F. Rahimpour, T. Shojaeimehr, M. A. Khadivi, M. Sadeghi, *J. Ind. Eng. Chem*., 20, 870 (2014)

[22] S. Çoruh, F. Geyikçi, E. Kılıç, U. Çoruh, *Bioresour. Technol*., 151, 406 (2014).