Artificial neural networks approach for modeling of Cr(VI) adsorption from aqueous solution by MR, MAC, MS

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ABSTRACT

The adsorption ability of Dowex Optipore L493 resin modified with Aliquat 336 (MR), activated carbon modified with Aliquat 336 (MAC), and sawdust modified with Aliquat 336 (MS) for removal of Cr(VI) from aqueous solution in batch system is investigated. The effects of operational parameters such as adsorbent dosage, initial concentration of Cr(VI) ions, pH, temperature, and contact time are studied. An artificial neural network (ANN) model is developed to predict the efficiency of Cr(VI) ions removal. The results reveal that the Langmuir isotherm fits better than the Freundlich isotherm. The rate of adsorption shows the best fit with the pseudo-second order model. Thermodynamic parameters show that the adsorption of Cr(VI) adsorption is feasible, spontaneous, and exothermic. The comparison of the removal efficiencies of Cr(VI) using ANN model and experimental results show that the ANN model can estimate the behavior of the Cr(VI) removal process under different conditions.

1 Introduction

There are various studies reported in the literature for the removal of heavy metals using large number of adsorbents (Shojaeimehr et al., 2014; Maheshwari et al., 2016; Siva Kiran et al., 2017; Asl et al., 2013; Yetilmezsoy et al., 2008; Turan et al., 2011; Mandal et al., 2015a; Oguz et al., 2014; Podstawczyk et al., 2015; Shanmugaprakash et al., 2013; Parveen et al., 2017; Mandal et al., 2015b; Oguz 2017; Gomez-Gonzalez et al., 2016; Oladipo et al., 2015; Prakash et al., 2008; Aber et al., 2009; Oguz et al., 2010; Singha et al., 2015; Turan et al., 2011; Yavuz et al., 2011). The presence of heavy metal ions in water and wastewater is considered as a major problem regarding toxicity, non-biodegrad-ability, and severe damages in human

health (Shojaeimehr et al., 2014). Chromium exists in the environment as trivalent and hexavalent forms. Although Cr(III) is an essential element for humans, water soluble Cr(VI) is highly irritating and toxic to humans and animals (Asl et al., 2013; Shanmugaprakash et al., 2013; Parveen et al., 2017; Mandal et al., 2015b; Aber et al., 2009; Gode and Pehlivan, 2003; Gode and Pehlivan, 2005a). WHO (World Health Organization) recommended a guideline value of 0.05 mgL^{-1} (desirable) for total chromium in drinking water with no relaxation on a permissible limit (Yavuz et al., 2011). Anthropogenic sources of chromium are used for general industrial processes such as electroplating, leather tanning, wood preservations, manufacturing of dye, paint and paper (Asl et al., 2013; Aber et al., 2009; Yavuz et al., 2011).

Several methods have been developed in order to remove heavy metal ions containing precipitation, electrochemical treatment, adsorption, ion exchange processes, solvent extraction, membrane systems, filtration (Shojaeimehr et al., 2014; Yavuz et al., 2011). With respect to all methods, adsorption is a common and effective method for heavy metal ions removal because of low cost, high efficiency, and good operational conditions. Numerous adsorbents such as zeolite (Asl et al., 2013), resin (Mandal et al., 2015b; Gode and Pehlivan, 2005a), lignite (Hassani et al., 2014; Gode and Pehlivan, 2005b), pumice (Turan et al., 2011), agricultural or industrial waste materials (Oladipo et al., 2015; Prakash et al., 2008; Siva Kiran et al., 2017; Yetilmezsoy et al., 2008; Shanmugaprakash et al., 2013; Parveen et al., 2017), and biomass (Oguz et al., 2014) have been studied for the capability of chromium and heavy metal removal from aqueous solutions. In the recent decade, many researches were conducted to access sorbents with higher efficiency and lower cost. The cost of adsorbent is an important parameter for comparison of adsorbents. In our study, solvent impregnated adsorbents named as MR, MAC and MS have been used. Dowex Optipore L493 resin is a highly cross-linked styrenic polymer that is insoluble in strong acid, strong base or organic solvents. It has a high surface area and a unique pore size distribution (Dincturk-Atalay, 2012). Activated carbon Calgon CPG has high mechanical strength and uniform transport pore distribution and a strongly adsorbing pore structure optimal for the adsorption. Sawdust is an industrial waste and low cost adsorbent (Dincturk-Atalay, 2012; Gode and Pehlivan, 2008).

The most important stage in an environmental process is modeling and optimization to improve a system and increase the efficiency of the process without increasing the cost (Shojaeimehr et al., 2014). The mechanism of adsorption processes is complex. This is due to the complex interaction of variables and the non-linear behavior of these processes. As a result, determination of optimum experimental condition is very important to obtain maximum efficiency. The classical optimization method (single variable optimiza-tion) is not only time-consuming and tedious but also does not depict the complete effects of the parameters in the process and ignores the combined interactions between physicochemical parameters. This method can also lead to misinterpretation of results. To overcome this difficulty, some statistical methods have been used. In recent years artificial neural networks (ANNs) have been widely studied to solve environmental problems because of their reliable and salient characteristics in capturing the non-linear relationships existing between variables(Shojaeimehr et al., 2014; Ghaedi et al., article in press; Siva Kiran et al., 2017; Karimi et al., 2016; Elemen et al., 2012). It can be used to solve problems that are not eligible for conventional statistical methods. ANNs have been considered because of wide spread uses and their capability and ability to solve complicated problems.

Examples for application of AANs in water treatment include Cu^{2+} removal by sawdust (Prakash et al., 2008), flax meal (Podstawczyk et al., 2015), Cu(II) adsorption with industrial leachate by pumice (Turan et al., 2011), Cr(VI) removal by solid biodiesel waste residue (Shanmugaprakash et al., 2013), cerium oxide polyaniline composite (Mandal et al., 2015b), zeolite (Asl et al., 2013) and clay (Shojaeimehr et al., 2014).

The main objective of this study is to evaluate the MR, MAC and MS adsorption capacity in chromium removal through the application of ANNs. The adsorptive removal of chromium depends on several parameters such as initial chromium concentration, adsorbent dosage, contact time, temperature and initial pH of the solution. Also the adsorption kinetic, equilibrium models, and thermodynamic studies as well as MR, MAC, and MS behavior as a sorbent in chromium removal are explained.

2 Materials and methods

2.1 *Adsorption experiments and instruments*

Cr(VI) stock solution (from Merck) was prepared from potassium salts of dichromate ($K_2Cr_2O_7$) of analyticalgrade. Double distillated water was used in all experiments. MR, MAC and MS were used as sorbents. The sorption mixture consisted of 0.1 g of sorbent inchromium solution from 1.0×10^{-4} to 2.5×10^{-3} mol/L $K_2Cr_2O_7$ for 2 h at 25 ± 2 °C in the batch experiments. After reaching equilibration, the sorbent solution was passed through a filter and analysed for chromium content using an atomic adsorption spectrometer (Perkin-Elmer AA800 Model). The effects of different chromium concentrations (1.0×10^{-4}-2.5×10^{-3} molL^{-1}), sorbent dosage (100-800 mg), contact time, pH (2-8) and temperature (25–65 ± 2 °C) using a thermostatic shaking water bath (MemmertWB29 Model) on chromium sorption were investigated. Solutions of 0.01M NaOH and HCl (from Aldrich) were used for pH adjustment. The pH was measured by using a glass electrode (Eutech Instruments Ion 510 Cyberscan model).

2.2 *Artificial neural networks (ANN)*

A feed-forward ANN model with three layers of nodes was constructed as in Fig. 1. The logistic function was used as the activation function in a neural network. The training and testing data sets must be normalized into a range 0.1-0.9. The input and the output data sets were normalized by using the following equation (Aktas and Yasar, 2004).

$$X_N = 0.1 + \frac{0.8\,(X - X_{min})}{(X_{max} - X_{min})}, \qquad (1)$$

where X_N is normalized value of a variable (the network input or the network output), X is an original value of the variable, and X_{max} and X_{min} are the maximum and the minimum original values of the variables, respectively. In order to produce sufficient data for training and testing of the model shown in Fig. 1, five different standard
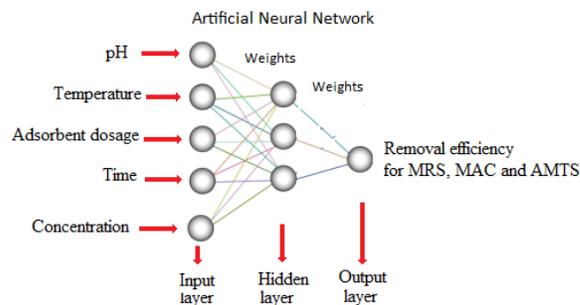

Figure 1. Artificial neural network architecture

solutions were prepared using 2.0 to 8.0 pH range, 25 to 65 °C temperature range, 100 to 800 mg adsorbent dosage range, 5 - 480 minute contact time range, and 1.0×10^{-4} - 2.5×10^{-3} M concentrations range, which were subject to neural network procedure. Randomly chosen 380 data pairs from these 545 data pairs were used for training the neural network, where the rest of the data were used for testing. The root mean square error values were calculated from the following equation to prove quantitatively the accuracy of the testing results of neural network models:

$$\text{RMS} = \sqrt{0.5\,N^{-1}\sum_{i=1}^{N}(X_1' - X_1)^2}, \qquad (2)$$

where N is the number of testing data and X_1' is target value.

3 Results and discussion

3.1 *Effect of pH on Cr(VI) removal*

Chromate ions exist in the aqueous solutions in different ionic forms (chromicacid (H_2CrO_4) and dichromate ($Cr_2O_7^{-2}$)), where the pH dictating of particular chromate species will predominate. In this process, the anion is not a simple monovalent anion but rather a series of chromate anions depending upon the pH and concentration of the solution. The total chromate species will be represented as Cr(VI) or chromate. The chromate may be represented in various forms such as H_2CrO_4, $HCrO_4^-$, CrO_4^{2-}, $HCr_2O_7^-$, and $Cr_2O_7^{-2}$in the solution phase as a function of pH and

concentration. In the neutral solution at low concentrations, Cr(VI) will be present in the form of $HCrO_4^-$ and CrO_4^{2-}. At acidic pH, $HCrO_4^-$ is the predominant Cr(VI) species in the aqueous phase. By reducing pH of the equilibrium solution, Cr(VI) uptake increases, only up to a certain pH, by forming more $HCrO_4^-$ at the expense of $Cr_2O_7^{-2}$. Once the pH value of about 3 is reached, the further reduction in pH will not increase the Cr(VI) uptake.

Hunt notes as a generalization, the binding of metal ions involvs two mechanisms, the first of these being simple ion exchange and the second through the formation of complexes, which may be chelates (Gode et al., 2008). Because of the complexity of most biomaterials, it is very likely that both of these binding processes will take place in a system at the same time. The interactions of chromium ions with MR, MAC, and MS surface molecules are complex, dominated by adsorption, ion exchange and chelation. The interaction of Cr(VI) with MR, MAC, and MS was investigated at different pH values. The pH value of the solution is an important factor that controls the sorption of Cr(VI). Adsorption of Cr(VI) was studied at different pH values to determine the optimum pH range, where the results are shown in Fig 2. The pH was adjusted with small additions of 0.1 M HCl or NaOH in the experiments. In order to find out the optimum pH for maximum removal efficiency, experiments were conducted by changing the pH of Cr(VI) solution from 2 to 8 at room temperature. From Fig. 2, decreasing the pH of the aqueous solution from 8 to 4, a distinct increase in the sorption is observed. The sorption of Cr(VI) ion on the sorbents is clearly very favorable at pH=2. As also seen in Fig. 2, the higher chromate removal capacity at the acidic pH is due to the removal of a greater number of Cr(VI) ions as per sorption site of the MR, MAC and MS. At higher pH values, greater than 6, the presence of OH−ions forms the hydroxidecomplexes of chromium (Gode and

Pehlivan, 2005a). Hexavalent chromium existing as negative species in the solution may release hydroxide (OH−) instead of proton (H+) when they are adsorbed by MR, MAC, and MS. This results in an increase of pH (Gode et al., 2008).
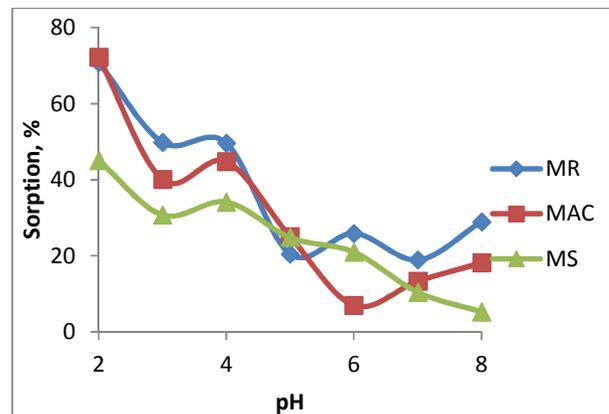

Figure 2. Effect of pH on the adsorption of Cr(VI) using MR, MAC, and MS.

For that reason, the uptake decreases at high pH values. The Cr(VI) is very soluble in aqueous solutions, where their solubility increases with pH; therefore, it was practical to employ adsorbents at solution pH values of 6 and below (Gode and Pehlivan, 2005a).

3.2 *Effect of Initial Cr(VI) Concentration and Adsorption Isotherms*

Factors influencing the adsorption rate are mainly, among others, the nature and concentration of competing ions, pH, sorbent amount, shaking speed, and temperature. Equilibrium isotherm, the relation between the amount exchange (qe), and the remaining concentration in the aqueous phase (Ce) are important to describe how solutes interact with the sorbents and so are critical in optimizing the use of the sorbents. The effect of sorbate concentration is shown in Fig. 3 as a function of the equilibrium concentration of metal ions in the aqueous medium at room temperature (25 °C) for 2 h of contact time. In the case of low Cr(VI) concentrations, the ratio of the initial number of moles of chromium ions to the available surface

area is smaller and subsequently the fractional adsorption becomes independent of the initial concentrations.
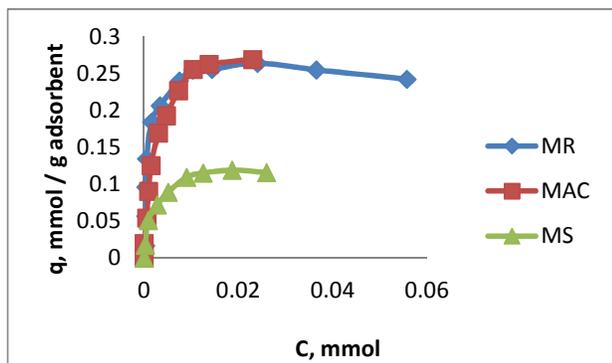

Figure 3. Sorption isotherms of Cr(VI) on MR, MAC, and MS as a function of the initial chromium concentration.

However, at higher concentrations, the available sites of adsorption become fewer, and hence the percentage removal of chromium ions depends upon the initial concentration. The amount of Cr(VI) ions adsorbed per unit mass of the MR, MAC, and MS increases with the initial chromium concentration as expected. To obtain maximum sorption capacities or reach the plateau values that represent saturation of the active groups which are available for interaction with Cr(VI) ions on the MR, MAC, and MS, the initial concentration was increased from 1.0×10^{-4} to 2.5×10^{-3} mol/L Cr(VI) for MR, MAC, and MS. All adsorbents were saturated at relatively low concentrations indicating strong binding for Cr(VI). The sorption capacities were 0.27, 0.28 and 0.28 mmol of Cr(VI) per g of MR, MAC, and MS, respectively. Langmuir, Freundlich (Eq. 3, 4) and Dubinin-Radushkevich (Eq. 5) adsorption isotherm models were tested to the adsorption data. The isotherm study provides information on the capacity of the adsorbent and characterization of the adsorption process was described by using a number of different isotherm models developed by researchers. The Freundlich equation is represented as

$$q = K_f \times C_e^n, \tag{3}$$

where n is the Freundlich constant and K_f is the adsorption coefficient, *q is* the weight adsorbed per unit weight of the adsorbent, and C_e is the equilibrium metal concentration in the fluid.

The Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites. The Langmuir isotherm is represented by the following equation:

$$Ce/qe = Ce/Q_0 + 1/Q_0 b, \tag{4}$$

where *C*e is the equilibrium concentration (mg/L), *q*e is the amount of adsorbed material at equilibrium (mg/g), *b* is the "affinity" parameter or Langmuir constant (L/mg), and Q_0 is the "capacity" parameter (mg/g)(Gode and Pehlivan, 2005a; Asl et al., 2013; Hassani et al., 2014; Karimi et al., 2016). The Langmuir constant *b* can serve as an indicator of isotherm rise in the region of lower residual chromium concentrations, which reflects the strength of the sorbent for the solute. The adsorption of Cr(VI) by sorbents is very high at low initial concentrations and reaches equilibrium very quickly. This indicates the possibility of the formation of monolayer coverage of the chromium ions at the outer interface of MR, MAC, and MS which suggests that these sorbents can remove most of the chromium ions from aqueous solution if their concentrations are low. Our experimental results obtained for the adsorption isotherms of MR, MAC, and MS were found to obey the Langmuir adsorption isotherms, as shown in Table 1.

Dubinin–Radushkevich isotherm: The linear form of D–R isotherm is represented by

$$\ln q_e = \ln q_m - k_{D-R}\varepsilon^2, \tag{5}$$

where q_m is the adsorption capacity (mg/g), k_{D-R} is the constant related to adsorption energy $(mol^2 kJ^{-2})$ and ε is the polanyi potential. The value of *k* is used to calculate the main free energy E (kJ mol^{-1}) of the sorption by using $E = -(2k)^{-0.5}$.

The calculated values of the D–R isotherm parameters for chromium ions are depicted in Table 1.

Table 1. Langmuir, Freundlich, and Dubinin –Radushkevich (D-R) adsorption parameters on MR, MAC, and MS adsorbents with Cr(VI).

Langmuir Adsorption Isotherm			Freundlich Adsorption Isotherm			
Sorbent	Q_o	b	R^2	K_f	n	R^2
MR	0.27	1234.2	0.999	1.47	2.83	0.995
MAC	0.28	600.8	0.992	1.47	2.50	0.887
MS	0.28	600.8	0.996	0.60	2.59	0.887
Dubinin–Radushkevich (D-R) Adsorption Isotherm						
Sorbent	q_m		k	E		R^2
MR	13.25		3.10^{-8}	4.08		0.977
MAC	12.84		1.10^{-8}	7.07		0.993
MS	28.18		3.10^{-8}	4.08		0.993

In Table 1; K_f and Q_o (mmol/g adsorbent) are the capacity of adsorbent, b and n are constants, qm (mmol/g) is the D-R adsorption capacity, k(mol2/kj-2) is a constant, E (kJ/mol) is the main free energy of adsorption, and R^2 is the correlation coefficient.

The values of *E* obtained from the D–R isotherm models for chromium ions found below 8 revealed the adsorption dominant of the process.

3.3 *Effect of MR, MAC and MS dosages*

The effects of variation of sorbent dosage on the removal of chromium by MR, MAC, and MS are shown in Fig. 4. Adsorbent dosage was varied from 100 to 800 mg and equilibrated for 2 h at an initial chromium concentration of 1.0×10^{-3} M. It is seen that the equilibrium concentration in the solution phase decreases with increasing adsorbent doses (Gode and Pehlivan, 2003).
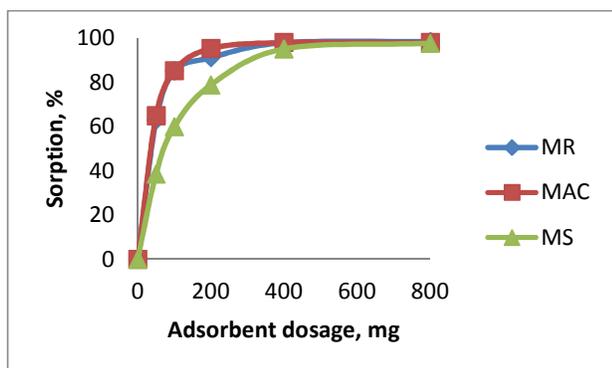

Figure 4. Effect of amount of adsorbents on the removal of Cr(VI) using MR, MAC, and MS

3.4 *Effect of time on removal of Chromium(VI)*

The contact time is one of the effective parameters in adsorption capacity. In the present paper, Fig. 5 illustrates the effect of shaking time on the removal by MR, MAC, and MS. High adsorption rates of chromium for all sorbents are observed at the onset, and then plateau values are gradually reached. It is obvious that Cr(VI) adsorption on MR, MAC, and MS was fast during the first 15 min. The increasing contact time increased the Cr(VI) adsorption where it remains constant after that the equilibrium is reached in 30 min for initial concentration of 1.0×10^{-3} mol/L.
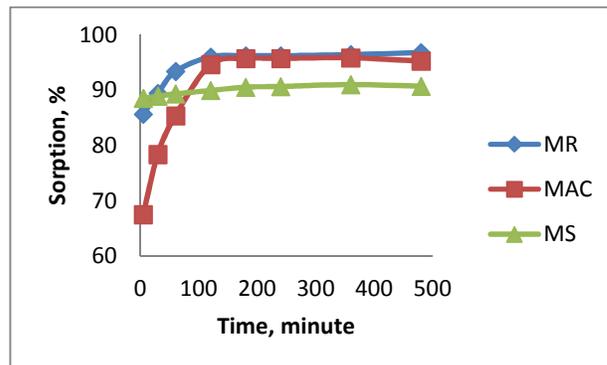

Figure 5. Effect of contact time on the adsorption of Cr(VI) using MR, MAC, and MS

The concentration of chromium in the solution decreased rapidly within 45–60 min and sorption was virtually completed within 80–120 min. As time passes, the adsorption capacity remained unchanged within the test duration. Then, 120 min was considered as the equilibrium time. It can be implied that during the initial stage, numerous vacant surface sites were available. By occupying the vacant surface sites by metal ions, the changes of adsorption capacity were decreased. The Cr(VI) adsorption with respect to time curves is single, smooth, and continuous leading to saturation showing monolayer coverage of chromium ions on the surface of the adsorbent (Gode and Pehlivan, 2003; Gode and Pehlivan, 2005; Asl et al., 2013; Hassani et al., 2014; Karimi et al., 2016). The adsorption of chromium ions in

aqueous solutions followed pseudo second order kinetics. The kinetic equations were calculated according to the known equation (Gok et al., 2007; Elwakeel 2010) where some constants were given in Table 2.

Table 2. Rate constants for the removal of Cr(VI) with MR, MAC and MS

Metal	Sorbent	$q_{e\text{-cal.}}$	k_2	$q_{e\text{-exp.}}$	R^2
Cr(VI)	MR	0.727	0.78	0.72	1
	MAC	0.724	0.34	0.71	0.99
	MS	0.327	4.26	0.32	1

In Table 2, $q_{e\text{-cal.}}$ (mmol/L) is the calculated amount from the adsorption equation, k_2(g/mg.minute) is the rate constant of the pseudo second order adsorption, $q_{e\text{-exp.}}$(mmol/L) is the amount of chromium adsorbed at equilibrium, and R^2 is the correlation coefficient.

3.5 *Temperature dependence of adsorption*

The thermodynamic parameters are studied to evaluate the inherent energetic changes of the system. The effect of the temperature on Cr(VI) adsorption by MR, MAC, and MS was investigated in this study at 25, 35, 45, 55 and 65 °C temperatures. The effect of temperature on the equilibrium constant (*K*c) for the adsorption of chromium ions onto MR, MAC, and MS was investigated. Equilibrium constants for Cr(VI) were high and adsorption increased slightly with temperature for MR and MAC. This is due to the exothermic adsorption reactions of Cr(VI) ion with MR and MAC. The equilibrium constants for such reactions slightly increase with temperature. According to our results, adsorption decreased slightly with temperature for MS. Assuming that the activity coefficients are unity at low concentrations, (the Henry's lawsense), thermodynamic parameters were calculated using the following relations (Asl et al., 2013; Hassani et al., 2014).

$$Kc = C_{Ae}/ C_e, \tag{6}$$

$$\Delta G° = -RT \ln Kc, \tag{7}$$

$$\log Kc = \Delta S°/2.303R - \Delta H°/2.303RT, \tag{8}$$

where *K*c is the equilibrium constant, C_e is the equilibrium concentration in solution (mg/L), and C_{Ae} is is the solid-phase concentration at equilibrium (mg/L). $\Delta G°$, $\Delta H°$, and $\Delta S°$ are changes in the free energy, enthalpy, and entropy, respectively. $\Delta H°$ and $\Delta S°$ were obtained from the linear Van't Hoff plot of log*K*c versus $1/T$ and presented in Table 3. Negative $\Delta G°$ values confirm the feasibility of the process and spontaneous nature of the adsorption with high preference of Cr(VI) for the MR, MAC, and MS. The negative values of $\Delta H°$ indicate the exothermic nature of the process while the negative $\Delta S°$ corresponds to a decrease in the degree of freedom of the adsorbed species (Gode and Pehlivan, 2003). Accordingly, the positive value of the enthalpy change confirms the endothermic nature of adsorption process for MS. This reveals the effect of temperature on the distribution coefficient, Kc, which increases with the increment of temperature. The value for $\Delta S°$ was found to be positive showing the tendency of MS to adsorb chromium ions and the randomness in the liquid/solid interface during the adsorption process. According to the values of $\Delta G°$ in Table 3, the Cr(VI) adsorption process onto MR, MAC, and MS is a physical adsorption process.

Table 3. Thermodynamic parameters for the adsorption of Cr(VI) on MR, MAC, and MS

Sorbents			ΔG					
	ΔH	ΔS	T_1	T_2	T_3	T_4	T_5	R^2
MR	-22938.3	-72.2	-3623.2	-2434.4	-2229.7	-2144.6	-2090.1	0.986
MAC	-21961.8	-69.9	-2114.6	-1985.9	-1699.5	-1708.4	-1571.4	0.941
MS	3934.7	8.8	-846.7	-515.9	-399.0	-346.6	-159.2	0.848

In Table 3, $\Delta G°$ (kJmol⁻¹) is the Gibbs free energy, $\Delta H°$ (kJmol⁻¹) is the enthalpy, $\Delta S°$ (kJmol⁻¹) is the entropy change, and R^2 is the correlation coefficient.

3.6 *Artificial neural network*

In order to provide the optimal model for removal efficiencies of MR, MAC, and MS adsorbents with Cr(VI) ions, the data were trained and tested for many times on 8 different models. These tests were performed with experimental data given for

training and testing. Prediction values for each of these resins were determined separately in training studies as the highest specificity coefficient and the lowest meansquare error. Matlab R2013a software carries out linear regression between regression button network inputs in training window and the outputs of these inputs. The results of MAC adsorbent are indicated in Fig. 6.
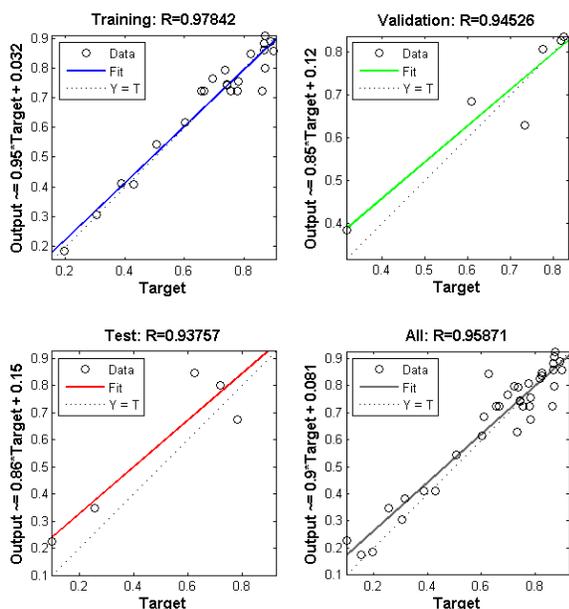

Figure 6. Network regression for MAC

It was observed in the figures that the training, verification, and test results were really good. Experimental data not shown in the network can also be simulated with this network architecture which has a quite high performance. The RMS values obtained for training, validation, and testing from the recommended artificial neural networks are given in Tables 4, 5 and 6.

Table 4. Comparison of the performances of the artificial neural networks models for MR

RMS errors			
Model	Training	Validation	Testing
NN 5-3-1	0.0085703	0.025476	0.0086158
NN 5-4-1	0.00543810	0.00706583	0.0136799
NN 5-5-1	0.00228955	0.0105867	0.00978704
NN 5-6-1	0.0379731	0.019380	0.0529241
NN 5-7-1	0.0835735	0.00660583	0.0198193
NN 5-8-1	0.00236900	0.00837764	0.00150158
NN 5-9-1	0.0034681	0.0014577	0.00659504
NN 5-10-1	0.0691919	0.00144311	0.000538225

Table 5. Comparison of the performances of the artificial neural networks models for MAC

RMS errors			
Model	Training	Validation	Testing
NN 5-3-1	0.00574923	0.00120710	0.0115904
NN 5-4-1	0.0120461	0.00908784	0.0128129
NN 5-5-1	**0.00206124**	**0.00365255**	**0.0154927**
NN 5-6-1	0.00309978	0.0302336	0.19939
NN 5-7-1	0.0109677	0.0131461	0.0224989
NN 5-8-1	0.00486029	0.00279180	0.00883566
NN 5-9-1	0.00455064	0.00374960	0.011477
NN 5-10-1	0.00247010	0.00471528	0.00582213

Table 6. Comparison of the performances of the artificial neural networks models for MS

RMS errors			
Model	Training	Validation	Testing
NN 5-3-1	0.0354174	0.00872118	0.0628209
NN 5-4-1	0.140054	0.0192388	0.373284
NN 5-5-1	0.0100908	0.0138513	0.0367470
NN 5-6-1	0.00650812	0.0198710	0.0285774
NN 5-7-1	0.0122588	0.0395477	0.0307165
NN 5-8-1	0.0124422	0.0462221	0.0543918
NN 5-9-1	0.00455177	0.00802429	0.0210923
NN 5-10-1	0.00122031	0.000539560	0.0551898

4 Conclusions

Adsorptive removal of chromium ions from aqueous solution using three different sorbents and the effects of different parameters (pH, initial chromium concentration, temperature, contact time and adsorbent dosage) on adsorption capacity in batch system have been reported. A neural network based model has been developed for the prediction of percentage removal of Cr(VI) ions from aqueous solution in a batch process using MR, MAC, and MS. The most important conclusions from the present study are summarized as follows:

- The optimum conditions were found at an initial pH of 2, temperature of 25 °C, initial chromium concentration of 1.0×10^{-3} M, and sorbent dosage of 200 mg.

- The results of ANN methodologies based on validation data showed that ANN is a useful and accurate method to predict adsorption process.

- Langmuir isotherm showed the best agreement with the equilibrium data than Freundlich isotherm.

- The thermodynamic studies proved that Cr(VI) removal using MR, MAC, and MS was a

spontaneous, feasible, exothermic and random process with mechanism of physical adsorption.

- The adsorption of chromium ions in aqueous solutions followed pseudo second order kinetics.

As a result; MR, MAC, and MS may be an alternative to expensive adsorbents where ANN methodology can be available.

Acknowledgements

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