

ORIGINAL ARTICLE

Fixed-bed column studies on the removal of Fe³⁺ and neural network modelling

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KEYWORDS

Fixed bed column; Fe³⁺; Ignimbrite; Neural network; Sorbent capacity **Abstract** The sorption potential of the particles of ignimbrite to uptake Fe³⁺ ions from an aqueous solution was investigated using a fixed-bed sorption column. The effects of inlet Fe³⁺ concentration (20–75 mg L⁻¹), feed flow rate (5–15 mL min⁻¹) and bed height (5–20 cm), initial solution pH (1.7–4) and particle size (0.25–0.5, 0.5–1 and 1–2 mm) on the breakthrough characteristics of the sorption system were investigated. The experimental and neural network sorption capacities of the sorbent at different particle sizes (0.25–0.5, 0.5–1, and 1–2 mm) were determined as 3.26, 3.75, 2.12, 2.98 and 1.46, 1.39 mg g⁻¹, respectively. The highest experimental and theoretical bed capacities were obtained to be 3.65 and 3.29 mg g⁻¹ at inlet Fe_o³⁺ concentration of 75 mg L⁻¹, bed height of 5 cm and flow rate of 5 mL min⁻¹, pH of 4 and particle size of 0.25–0.5 mm. The ANN model yielded determination coefficient was 0.980 and the root mean square error was 0.65.

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1. Introduction

One of the most commonly used metals in the world metal production is iron because of its low price and hardness. Excessive concentrations of Fe^{3+} in public water supplies cause turbidity, unpleasant taste and odour. It imparts a brownish colour to laundered cloths and stains plumbing fixtures. It also causes difficulties in distribution systems by supporting the growth of iron bacteria, resulting in the clogging of pipes (Onganer and Temur, 1998). Therefore, the presence of Fe^{3+} is objectionable

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in certain industries such as food, textiles and paper (Sag and Kutsal, 1996). While Fe^{3+} is found naturally in large concentrations in an insoluble form, it can be converted to soluble forms that often result in water contamination (Indianara et al., 2009).

At present, various traditional treatment technologies including chemical precipitation, filtration, ion exchange and activated carbon adsorption on a solid heterogeneous surface are widely applied and have been developed (Khan et al., 2007; Peters and Ku, 1984; Kanzelmeyer and Adama, 1996; Gode and Pehlivan, 2003; Aksu and Alperis, 2005). These methods, however, display one or more limitations, such as being ineffective, expensive, generation of secondary pollution and narrow appliance range. In order to overcome these limitations, chemists have been devoted to searching for effective, economic and easily implemented materials (Pehlivan and Arslan, 2007; Khan et al., 1995; Keane, 1998; Gupta and Ali, 2000; Gupta and Rastogi, 2008).

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Adsorption is an attractive method because it is easy to operate and is highly effective in removing heavy metals from effluents (Popuri et al., 2009). However, the utilisation of commercialised adsorbents like activated carbon is expensive, which leads to high operational costs (Tor et al., 2009). Research on low-cost, natural adsorbents such as montmorillonite, agricultural waste and seafood processing waste has recently gaining ground due to their availability, short operational time and non-generation of sludge.

Ignimbrite, which is a building material, is included in the light concrete category. One of the main advantages of Fe^{3+} removal by using ignimbrite particles over the other chemical treatment methods is that it does not produce any chemical sludge. In addition, after ignimbrite has been used in building works, its residues can easily be used to remove Fe^{3+} from aqueous solutions. In the present study, an attempt was made to investigate the Fe^{3+} removal potential of ignimbrite particles under different environmental conditions. Ignimbrite is an economical rock, and is included in the light concrete category.

The chemical components of ignimbrite consist of SiO₂, Fe₂O₃, Al₂O₃, CaO, MgO, K₂O and other components (Aydin et al., 2010). An important advantage of ignimbrite is its occurrence in active fault zones all over the world. These rocks are widely used as building stones in low storeyed buildings and especially in important buildings in the past. Nowadays, they have an increasing usage in outer surface coverings of the buildings, stairs, floorings, banisters, pools and their surroundings, arches, columns, fireplaces, balcony decorations and restoration applications because of their decorative properties (Korkanc, 2007). One of the main advantages of Fe³⁺ removal using ignimbrite over the other chemical treatment methods is that no chemical sludge is produced after sorption.

In practice the column type continuous flow operations, which are more useful in large-scale wastewater treatment, have distinct advantages over batch treatment. It is simple to operate, attain a high yield and it can be easily scaled up from a laboratory-scale procedure. The stages in the separation process can also be automated and high degrees of purification can often be achieved in a single step process. A packed bed is also an effective process for sorption/desorption, as it makes the best use of the concentration difference known to be a driving force for sorption and allows more efficient utilisation of the sorbent capacity and results in a better quality of the effluent. A large volume of wastewater can be continuously treated using a defined quantity of sorbent in the column (Valdman et al., 2001; Zulfadhly et al., 2001; Robinson et al., 2002; Rozada et al., 2003; Oguz and Ersoy, 2010).

The purpose of this study is to remove Fe^{3+} ions by the particles from aqueous solution using a fixed-bed sorption column. The effects of flow rate, pH value, influent concentration, bed depth and particle size on metal uptake by the particles of ignimbrite in a fixed bed column were investigated. A model based on an artificial neural network (ANN) has been constructed to model Fe^{3+} concentration removed from an aqueous solution as a function of empirical parameters.

2. Materials and methods

2.1. Sorbent preparation

The ignimbrite particles were cut into small pieces, ground in a blender and sieved to obtain particle sizes of 0.25 < x < 0.5,



Figure 1 Schematic diagram of experimental set up: (1) feed tank; (2) peristaltic pump; (3) fixed bed of the particles of ignimbrite; (4) bed support; (5) sampling port measuring Fe^{3+} concentration and (6) effluent collector.

0.5 < x < 1 and 1 < x < 2 mm. Ignimbrite samples were washed with distilled water and then dried at 298 K for two weeks. Samples of 7 g were taken for sorption studies.

 Fe^{3^+} solutions were prepared by diluting 483 mg L⁻¹ of $\mathrm{Fe}\mathrm{Cl}_3.6\mathrm{H}_2\mathrm{O}$ (Merck) stock solution with deionised water to a desired concentration range between 20 and 75 mg L⁻¹. The initial concentration of Fe^{3^+} and the samples following the sorption process were complexometrically determined.

The surface area of the particles of ignimbrite was measured by the BET method at 77 K using a Quantachrome QS-17 model apparatus (Brunauer et al., 1938). The surface area of the particles of ignimbrite was $2.90 \text{ m}^2/\text{g}$.

2.2. Fe³⁺ analysis

A sample of 5 mL that has a concentration less than 20 mg $Fe^{3+}/100$ mL was added to 10 mL of 1% sulphosalicylic acid and a few drops of 25% aqueous ammonia solution to keep the value of pH between 2.1 and 3.3, and then diluted to 50 mL with distilled water. The content of Fe^{3+} was determined by titration with 0.05 M EDTA solution. 1 mL, 0.05 M EDTA solution is equivalent to 2.792 mg Fe^{3+} (Gulensoy, 1984).

2.3. Column experiments

Continuous flow sorption experiments were conducted in Teflon columns of 1 cm i.d. and 5, 10, 15 and 20 cm heights as seen from Fig. 1. A known quantity of sorbent was placed in the column to receive the desired bed height. Fe³⁺ solution with an initial concentration of 50 mg L⁻¹ was pumped upward through the column at a desired flow rate by a peristaltic pump. Samples were collected from the exit of the column at different intervals and analysed for Fe³⁺ concentration. Operation of the column was stopped when the effluent Fe³⁺ concentration equals approximately influent Fe³⁺ concentration.

The total quantity of metal sorbated in the column was calculated from the area above the breakthrough curve (outlet metal concentration versus time), multiplied by the flow rate. Dividing the metal mass by the sorbent mass (M) leads to the uptake capacity (Q) of the sorbent. The total amount of

metal ions sent to the column can be calculated from (Eq. (1)) (Aksu et al., 2007).

$$m_{\text{total}} = \frac{C_o F t_e}{1000} \tag{1}$$

where C_o is the inlet metal ion concentration (mg L⁻¹), *F* the volumetric flow rate (mL min⁻¹) and t_e is the exhaustion time (minute). The mass transfer zone can be calculated from the difference between column exhaustion time (t_e) and column breakthrough time (t_b). The total metal removal (%) with respect to flow volume can be calculated from the ratio of metal mass sorbated (m_{ad}) to the total amount of metal ions sent to the column, given by (Eq. (2)) (Uddin et al., 2009).

Total metal removal (%) =
$$\frac{m_{\rm ad}}{m_{\rm total}} \times 100$$
 (2)

The amount of metal retained in the column depends on the influent metal concentration and can be calculated from the area above the breakthrough curve (Eq. (3)) (Hana et al., 2009).

$$q = \frac{C_o F}{m * 1000} \int_0^t \left(1 - \frac{C_t}{C_o} \right) dt \tag{3}$$

where q represents the amount of metal retained (mg of Fe³⁺ per g of sorbent), C_t and C_o are the Fe³⁺ concentrations at the column effluent and influent (mg L⁻¹) respectively, F is the flow rate (mL min⁻¹), m is the mass of sorbent in the column (g) and t is the sorption time (minute).

3. Results

3.1. The Effect of experimental conditions on the breakthrough curve

3.1.1. Effect of initial iron concentration

The effect of influent Fe_o^{3+} concentration on the shape of the breakthrough curves is shown in Fig. 2. As shown in Fig. 2, in the interval of 100 min, the value of C_t/C_o reached 0.23, 0.53 and 0.77 when influent concentration was 20, 50 and 75 mg L⁻¹, respectively.

It is illustrated in Fig. 2 that the breakthrough time decreased with the increase of influent Fe_o^{3+} concentration.



Figure 2 Experimental and theoretical breakthrough curves of Fe^{3+} as a function of inlet Fe^{3+} concentration (*T* 15 °C, pH 4, flow rate 5 mL min⁻¹, bed depth 5 cm, particle size 0.25–0.5 mm).

At lower influent Fe_{o}^{3+} concentration, the breakthrough curve was dispersed and breakthrough occurred slower. As the influent concentration increased, sharper breakthrough curves were observed. These results demonstrate that the change of concentration gradient affects the saturation rate and breakthrough time. These results also show that the change of concentration gradient affects the saturation rate of the sorbent and breakthrough time, in other words, the diffusion process is concentration dependent. As the influent concentration increases, Fe_{o}^{3+} loading rate increases, so does the driving force for mass transfer, in which the sorption zone length decreases (Goel et al., 2005).

3.1.2. Effect of flow rate

The effect of flow rate on the sorption of Fe^{3+} in the fixed-bed with bed depth of 5 cm was investigated. The flow rate was changed in the range of 5–15 mL min⁻¹, while the concentration of Fe^{3+} in influent was kept constant at 50 ppm. The sorption breakthrough curves obtained at different flow rates are shown in Fig. 3.

The obtained results show that the adsorption of Fe^{3+} on the particles of ignimbrite was strongly influenced by the flow rate. All the breakthrough curves had a similar shape. The breakthrough curves shifted to the origin with increasing flow rate, and an earlier breakthrough time and saturation time were observed for a higher flow rate. Fig. 3 shows that Fe^{3+} concentration in the effluent increased rapidly after the breakthrough time, as the solution continued to flow, the fixed-bed became saturated with Fe³⁺, and Fe³⁺ concentration in the effluent approached the influent concentration. Both equilibrium uptake and total removal efficiency of Fe³⁺ decreased with increasing flow rate, and their maximum value was obtained at the lowest flow rate of 5 mL min⁻¹. As shown in Fig. 3, in the interval of 100 min, the value of C_t/C_o reached 0.53, 0.97 and 0.99 when flow rate was 5, 10 and 15 mL min⁻¹, respectively.

3.1.3. Effect of bed depth

Another important parameter in the sorption process is relevant to the bed depth. However, because of the pressure drop and the handling problems of the smaller particle size < 0.25-0.5 mm in the column studies, the particle sizes of



Figure 3 Experimental and theoretical breakthrough curves of Fe^{3+} as a function of flow rate (*T* 15 °C, pH 4, C_o 50 mg L⁻¹, bed depth 5 cm, particle size 0.25–0.5 mm).

1-2 mm were used to compare C_t/C_o with sorbent capacities for the bed depths of 5, 10, 15 and 20 cm.

The retention of metals in a fixed-bed column depends, among other factors, on the quantity of sorbent used or, on the bed depth of the column works. The sorption performance of the particles of ignimbrite was investigated at various bed heights of 5, 10, 15 and 20 cm at a flow rate of 5 mL min⁻¹ where the inlet Fe_o^{3+} concentration was kept constant at 50 ppm. Fig. 4 shows the breakthrough profile of Fe^{3+} sorption at different bed heights. For the four different bed depths used, as the bed depth increases, the quantity of the removed Fe^{3+} concentration increases, which is also illustrated by the service time change.

As shown in Fig. 4, in the interval of 100 min, the value of C_t/C_o reached 0.97, 0.60, 0.21 and 0.00 when bed depth was 5, 10, 15 and 20 cm, respectively. At the column depth with 5 cm, the sorbent becomes saturated very quickly because saturation at the binding sites is faster.

3.1.4. Effect of pH

The pH value of the solution is an important controlling parameter in the sorption process, and the pH value of aqueous solution has more influence on uptake of Fe³⁺ ions in the fixed bed. It influences both the sorbent surface metal binding sites and the metal chemistry in water. When the pH of the feed solution was changed from 1.7 to 4, the highest sorbent capacity and the longest breakthrough time was achieved at pH 4. As shown in Fig. 5, in the interval of 100 min, the value of C_t/C_o reached 0.98, 0.80 and 0.53 when pH value of the solution was 1.7, 3 and 4, respectively. At the column depth with 5 cm, the sorbent becomes saturated very quickly because saturation at the binding sites is faster.

The pH of the aqueous solution is also an important controlling parameter in the sorption process. At pH between 3 and 4, there are three species present in the solution as suggested by Araujo et al., 2007. The dominant species between pH 3 and 4 were $Fe(OH)^{2+}$, $Fe(OH)^+_2$ and $Fe(OH)_3$. These species are sorbated in an electrostatic and chemical interaction on the surface of the shells. At low pH, the surface charge becomes positive due to high concentration of H_3O^+ ions. Very low sorption effectiveness at low pH is likely due to competition for binding sites with protons. Their presence



Figure 4 Experimental and theoretical breakthrough curves of Fe^{3+} as a function of bed depth (*T* 15 °C, pH 4, C_o 50 mg L⁻¹, flow rate 5 mL min⁻¹, particle size 1–2 mm).



Figure 5 Experimental and theoretical breakthrough curves of Fe^{3+} as a function of pH of solution (*T* 15 °C, bed depth 5 cm, C_o 50 mg L⁻¹, flow rate 5 mL min⁻¹, particle size 0.25–0.5 mm).

inhibits sorption, as the Fe^{3+} competes with protons to form a bond with active sites of functional groups on the sorbent surface. As the pH decreases, the surface of ignimbrite particles exhibits an increasing positive characteristic.

These species are sorbated with electrostatic interaction at the surface of the particles of ignimbrite. As the pH decreases, the particles of ignimbrite exhibit an increasing positive characteristic, thus breakthrough time decreased. Obviously with an increase of pH in the influent, the breakthrough curves shifted from left to right, which indicates that more metal ions can be removed.

As can be seen from Fig. 6, zeta potential values of the ignimbrite particles at pH (1.7–4) in the distilled water were smaller than these of Fe^{3+} solution. The dominant species in the Fe^{3+} solution were electrostatically affected by sorbent particles and then sorbated on the surface of the sorbent. Sorption of Fe^{3+} on the sorbent caused an increase of the zeta potential values. The increase in the zeta potential values of the sorbent was a sign of sorption of Fe^{3+} from aqueous solutions.

3.1.5. Effect of particle size

Another important parameter in the sorption process is related to the particle size of the sorbent. The particle sizes were 0.25-0.5, 0.5-1 and 1-2 mm, while the bed depth, influent



Figure 6 Relation between zeta potentials and pH.



Figure 7 Experimental and theoretical breakthrough curves of Fe^{3+} as a function of particle size (*T* 15 °C, bed depth 5 cm, C_o 50 mg L⁻¹, flow rate 5 mL min⁻¹, pH 4).

 Fe^{3+} concentration and pH were kept constant at 5 cm, 50 mg L⁻¹ and 4, respectively. The breakthrough curves concerning the particle size are given in Fig. 7.

An increase in the particle size appeared to increase the sharpness of the breakthrough curve. Furthermore, the sorption capacity for the larger particle size is lower than that for the smaller particle size. A rapid decrease in the column adsorption capacity with an increase in the particle size was observed. The clear shift of the breakthrough curve was obtained from 0.25–0.5 to 1–2 mm. This is mainly true due to the higher surface area of the smaller particle size. Therefore, a higher sorption capacity and shorter intraparticle diffusion path are expected. As shown in Fig. 7, in the interval of 100 min, the value of C_t/C_o reached 0.53, 0.80 and 0.97 when the particle size was 0.25–0.5, 0.5–1 and 1–2 mm, respectively.

4. Application of the artificial neural network

A linear model is not suitable to constitute a satisfying relationship among the input variables for a sorption process. In fact, it is reasonable to consider that such variables are not totally independent. The ANN approach seems to be completely suitable to the problems where the relations between variables are not linear and complex (Bernard et al., 2004).

A neuron sums the product of each connection weight (w_{jk}) from a neuron (j) to the neuron (k) and, input (x_j) and the additional weight called the bias to get the value of sum for the neuron. The *i*th neuron has a summer that gathers its weighted input $w_{ij}p_j$ and the bias b_i to form its net input n_i , which is given by (Eq. (4)):

$$n_i = \sum w_{ij} x_j + b_i \tag{4}$$

where w_{ij} denotes the strength of the connection from the *j*th input to the *i*th neuron, x_j is the input vector, b_i is the *i*th neuron bias. The sum of the weighted inputs is further transformed with a *transfer function* to get the output value. There are several transfer functions; the most common is the sigmoidal function (Yang and Wei, 2006; Oguz et al., 2008a,b). To find suitable w_s and biases for each neuron, a process training is essential; it is the first step to build an ANN. Training means that the weights are corrected to produce prespecified ("correct", known from experiments) target values, and the training

requires sets of pairs (X_S, Y_S) for input: the actual input into the network is a vector (X_S) , and the corresponding target is labelled (Y_S) after successful training. When correct values of Y_S for each vector of X_S from the training set are obtained, it is hoped that the network will give correct predictions of Y for any new object of X according to the ANN model fundamentals and with the use of more data for training the network, better result would be obtained. The most utilised training method for multilayered neural network is called *back propagation* (Kumar et al., 2005; Oguz and Ersoy, 2010; Oguz and Ersoy, 2014).

Information about errors (differences between the target and predicted values) is filtered back through the system and is used to adjust the connections between the layers, therefore performance improves. In the early standard algorithm, a random initial set of weights were assigned to the neural network, and then by considering the input data, weights were adjusted, so the output error would be the minimum (Sozen et al., 2004). In this study, one-layered back propagation neural network was used for modelling of the uptake of Fe^{3+} ions from aqueous solutions Fig. 8.

The input variables to the neural network are as follows: pH, the sorption time (t), the concentration of initial Fe^{3+} , bed depth (B.D.), flow rate (F) and particle size (P.S.) and Fe_o^{3+} concentration as a function of reaction time was chosen as the experimental response or output variable. In order to model the Fe_t^{3+} concentrations with ANN, the Statistica software programme was used. The coefficient of Root Mean Square Error (RMSE) is the main criterion to evaluate the performance of ANN, which is defined as follows:

$$RMSE = \sqrt{\frac{(obs - pre)^2}{n}}$$
(5)

A low value of the RMSE satisfies the statistical evaluation of prediction for the validation (Celik and Tan, 2005; Tortum, 2003). From Fig. 8, it can be observed that the newly constructed neural network was precise in predicting the Fe^{3+} uptake with a high correlation coefficient of 0.980. This shows that the developed neural network model can be precise in predicting the removal of Fe^{3+} by the particles of ignimbrite for the range of experimental conditions (Kumar et al., 2008).

Before the network was trained, the input and the output data were normalised. The scale and shift factors used in each input and output are given in Table 1.

The weight coefficients and the biases given in Table 2 are the values obtained for the normalised data in order to



Figure 8 The architecture of the ANNs used in this study.

Table 1	Shift and s	scale factors.	
Parameters		Shift	Scala
t		-0.019	0.004
$C_{\rm in}$		-0.363	0.018
pН		-0.739	0.435
P.S.		-0.333	0.888
B.D.		-0.333	0.066
F		-1.000	0.166
Cout		0.000	1.009

Table 2	Connection v	veights and	d biases.		
Bias	2.1	2.2	2.3	2.4	3.1
	b_1				b_2
	1.444	-0.228	0.423	-0.004	0.013
	w_1				
1.1	-0.879	-4.919	-0.319	1.782	
1.2	-0.1339	-0.935	-0.412	0.216	
1.3	0.104	2.000	-0.011	-0.471	
1.4	0.353	-1.075	-0.012	0.068	
1.5	0.135	2.740	0.208	-0.717	
1.6	1.247	-1.571	0.175	-0.683	W2
2.1					-0.624
2.2					-0.658
2.3					0.010
2.4					-0.297

Table 3	Sensitivity analysis results.						
	t	C_o	pН	P.S.	B.D.	F	
Ratio	10.03	1.93	4.00	3.79	6.27	3.18	
Rank	1	6	3	4	2	5	

determine the actual (experimental) Fe_t^{3+} concentration. An inverse transformation on these data is performed by using shift and scale factors. After long training phases, the best result was obtained from the Levenberg–Marquardt algorithm.

The hyperbolic tangent function in the hidden layer and the linear activation function in the output layer were used in the model. It was observed that the optimal network was found to have six inputs, one hidden layer with four neurons and one output layer. The optimal network architecture (6:6-4-1:1) is shown in Fig. 8.

Sensitivity analysis is a useful technique to assess the relative contribution of the input variables to the performance of a neural network by testing the neural network when each input variable is unavailable. This indicates that the input variables are considered to be the most important ones by a particular neural network. If the ratio is one or lower, the input variable has no effect on the performance of the network. Otherwise, when ratios of input parameters are more than one, all input variables are meaningful. The results of the sensitivity analysis are given in Table 3.

It can be seen from Table 3 that the most important parameters that affect the removal of the Fe_t^{3+} are sorption time (*t*), bed depth (B.D.), pH, particle size (P.S.), flow rate (*F*) and initial Fe_o^{3+} concentration (C_o), respectively.

Before training the network, both the input and output variables were normalised within the range of 0-1 using a minimax algorithm. The minimum and maximum of the data set were found and scaling factors were selected so that these were mapped to the desired minimum and maximum values.

The number of experimental data used in the ANN is 586, which were divided into three sections: the training set (294 data), verification set (146 data) and test set (146 data). Training algorithms do not use the verification or test sets to adjust network weights. The verification set may optionally be used to track error performance of the network to identify the best network and to stop training, if over-learning occurs. The test set is not used in training at all, and it is designed to give an independent assessment of the performance of the network when the design procedure of an entire network is completed. The assignment of the cases to the training, verification and test subsets can sometimes affect the performance of the training algorithms. In order to eliminate this drawback, the cases should be shuffled randomly between subsets. The cases can be left in their original order or grouped together in the subsets. In this model, the cases were shuffled randomly between the subsets (training, test and verification). The experimental and predicted sorbent capacities are given in Table 4.

The prediction of breakthrough curves was obtained using the Neural Network model. The Neural Network model provided a

C _o (ppm)	pН	F. rate (mL min ⁻¹)	P. size (mm)	B. depth (cm)	Bed capacity (mg g^{-1})		R^2
					Exp.	N. net.	
20	4	5	0.25 < x < 0.5	5	1.73	1.68	0.99
50	4	5	0.25 < x < 0.5	5	3.26	3.13	0.99
75	4	5	0.25 < x < 0.5	5	3.65	3.39	0.99
50	4	5	0.25 < x < 0.5	5	3.26	3.75	0.99
50	3	5	0.25 < x < 0.5	5	2.32	2.99	0.99
50	4	5	0.25 < x < 0.5	5	3.26	3.13	0.99
50	4	10	0.25 < x < 0.5	5	3.23	3.73	0.97
50	4	15	0.25 < x < 0.5	5	3.14	2.58	0.99
50	4	5	0.25 < x < 0.5	5	3.26	3.75	0.99
50	4	5	0.5 < x < 1	5	2.12	2.98	0.98
50	4	5	1 < x < 2	5	1.46	1.39	0.99
50	4	5	1 < x < 2	10	1.49	1.48	0.99
50	4	5	1 < x < 2	15	1.52	1.55	0.99
50	4	5	1 < x < 2	20	1.58	1.58	0.99

 Table 4
 Observed and predicted sorbent capacities at different experimental conditions.



Figure 9 (a) Comparison between observed and predicted values relating to general modelling (R^2 0.99), (b) residuals vs. predicted values, (c) relative error distribution, (d) normal probability plot of residuals.

good correlation in the prediction of the breakthrough curves due to its acceptable R^2 values (0.99–0.98), as well as a good agreement was observed between the simulated breakthrough curves and the experimental data points. The Neural Network model was used in predicting the theoretical breakthrough concentrations at different flow rates, pHs, particle sizes, bed depths and influent concentrations. The predicted values at different experimental conditions were in good agreement, as seen in Table 4.

In the ANN modelling, it was seen that the error distributions of the model did not show complete normal distribution. Almost every value predicted in the model and the distribution of the errors is very close to the zero line as seen in Fig. 9.

Error distributions do not show complete normal distribution. It was also observed that almost every value predicted in the model and the distribution of the errors was not in the line of zero. Every value predicted in the model and the distribution of the errors is very close to the zero line. The error histogram is not widely open to the right and left directions. The zero error frequency is high and also in the model the predicted values together with the observed values are in good agreement, as seen from Fig. 9. Furthermore, the explanatory variables in the models to explain the dependent variable are found to be satisfactorily sufficient. In a good model, the residuals show normal distribution. The assumption of normality can be checked by plotting the residual versus expected normal values. The normal probability plot of the residuals for ANN is shown in Fig. 9 which shows an approximately linear behaviour, indicating that the residuals follow an approximately normal distribution. The comparison between experimental and simulated data from the ANN belonging to all of the parameters is given in Fig. 9.

5. Conclusion

The particles of ignimbrite were used to define the experimental and theoretical sorbent capacities in a fixed bed column. The

 C_t/C_o , q_{exp} and q_{cal} are a function of the sorption time, bed depth, flow rate, sorbate concentration, sorbent particle size and pH. An artificial neural network modelling has been used to investigate relation between the cause and effect in the sorption studies of Fe³⁺ ions. The ANN model could describe the behaviour of the sorption with the adopted experimental conditions. A simulation based on the ANN model has then been performed in order to estimate the behaviour of the system under different conditions. The model based on the ANN has predicted the concentrations of Fe_t^{3+} uptake in a fixed bed column during the sorption time. A relationship between predicted and observed data has been constructed. In the ANN model, the value of root mean square error was obtained to be 0.65. According to the sensitivity analysis results, the most important parameters affecting the sorbent capacity were found to be sorption time, bed depth, pH, particle size, flow rate and initial $\operatorname{Fe}_{o}^{3+}$ concentration (C_{o}), respectively.

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