



Research Journal of
**Environmental
Sciences**

ISSN 1819-3412



Academic
Journals Inc.

www.academicjournals.com



Research Article

Artificial Neural Network (ANN) Approach for Modeling of Sr(II) Adsorption from Aqueous Solution by Natural Calcium-based Materials

^{1,2}Aysun Bulut, ¹Sabriye Yusan, ¹Sule Aytas, ¹Senol Sert and ³Oguz Akpolat

¹Institute of Nuclear Sciences, Ege University, 35100 Bornova, Izmir, Turkey

²School of Pharmacy, Altinbas University, Istanbul, Turkey

³Department of Chemistry, Mugla Sitki Koçman University, 48000 Kötekli, Mugla, Turkey

Abstract

Background and Objective: Nuclear pollution-causing strontium affects almost all life forms in the surrounding environment. This study aimed to investigate and explore the possibility of using eggshell powder (ES) and natural hydroxyapatite (HAp) derived from chicken bone for adsorption of Sr(II) ions from aqueous solutions. **Materials and Methods:** Eggshells and leg bones of the chicken were collected from the local market of Turkey. The Sr(II) removal from aqueous solutions by natural calcium based materials were studied in a batch mode. Adsorption isotherms (Langmuir, Freundlich and Dubinin-Radushkevich (D-R)) and thermodynamic parameters were calculated and obtained data were evaluated. The artificial neural networks (ANN) are carried out for prediction of adsorption efficiency for the removal of Sr(II) ions from aqueous solution by eggshell (ES) and bone ash-hydroxyapatite (BA-HAp). **Results:** Experimental results indicated that adsorption of Sr(II) was highly pH dependent and strontium removal at relatively high at pH 5 for BA-HAp and pH 6 for ES. The Freundlich and D-R equations are in quite an agreement with the equilibrium isotherm for these adsorbents. Thermodynamic studies indicated that the adsorption is physical, which is consistent with the results of the isotherm models. **Conclusion:** The natural calcium based adsorbents seems to be a suitable low-cost material for removing strontium ions from aqueous solutions. In addition, ANN model is an effective technique in modeling, estimation and prediction of adsorption process for Sr(II) ions onto ES and BA-HAp.

Key words: Eggshell, hydroxyapatite, strontium, adsorption, artificial neural networks

Citation: Aysun Bulut, Sabriye Yusan, Sule Aytas, Senol Sert and Oguz Akpolat, 2018. Artificial neural network (ANN) approach for modeling of Sr(II) adsorption from aqueous solution by natural calcium-based materials. Res. J. Environ. Sci., 12: 121-131.

Corresponding Author: Sabriye Yusan, Institute of Nuclear Sciences, Ege University, 35100 Bornova, Izmir, Turkey
Tel: +90 232 3113493 Fax: +90 232 3886466

Copyright: © 2018 Aysun Bulut *et al.* This is an open access article distributed under the terms of the creative commons attribution License, which permits unrestricted use, distribution and reproduction in any medium, provided the original author and source are credited.

Competing Interest: The authors have declared that no competing interest exists.

Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

The increased use of nuclear power plants and nuclear laboratories is the source of radioactive waste released to the environment¹. Strontium ions are one of the most abundant and toxic radio nuclides present in radioactive liquid wastes due to its complexity and long physical half life. Sr ions are bone-seeking element and have thus carcinogenic effects². Accordingly, it is very important to separate the Sr(II) ions from the wastewaters.

There are many techniques for removing metal ions from aqueous solutions^{2,3}. Among various treatment methods adsorption process is one of the most effective and economically feasible alternative methods used to remove metal ions from waste solutions. In order to remove Sr ions from aqueous solutions, organic and inorganic adsorbents have been widely employed⁴⁻¹⁰. New cost-effective, easily available and highly functional adsorbents are still under development. Hence, the present study attempted to develop inexpensive adsorbents for wastewater treatment processes which use eggshell and chicken bone powder. The mechanism of adsorption is also highly complex and difficult to model and simulate using conventional mathematical modelling due to the interaction of more number of adsorption process variables¹¹.

The ANN is one of the data based non-traditional tools for modeling of the adsorption process. This modeling contains a series of mathematical correlation which are used to simulate the learning and memorizing process. This technique learns through a set of input factors measured experimentally to determine the rules governing the relationship between variables and an example of the relevant outputs¹². The removal efficiency of the adsorbent is to be considered an output layer and the adsorption parameters such as pH, time, initial concentration, temperature etc., are to be considered an input layer of the ANN model. This modelling is very useful because of its simplicity towards simulation, prediction and less time according to traditional mathematical models¹¹. In the literature, ANN model has been applied for sorption studies with promising results¹¹⁻¹⁷.

In the literature it can be found, there are few studies relating to removal of strontium from aqueous solutions using bone ash¹⁸ and eggshell powder¹⁹. These studies are limited in the literature although there is no study about the artificial neural networks was used for modeling of adsorption of Sr(II) from aqueous solutions by eggshell and bone ash.

The objective of the study is to investigate and explore the possibility of using eggshell powder and natural HAP derived from chicken bone for adsorption of Sr(II) ions from

aqueous solutions. The effects of pH, initial Sr(II) concentration, contact time and temperature on strontium adsorption were investigated and ANN model is used to predict the Sr(II) removal efficiency of ES and BA-HAP used as low cost adsorbents are applied in this work. Characterization of the samples, adsorption isotherms and thermodynamic parameters were also assessed and reported.

MATERIALS AND METHODS

Materials: In this study, all chemicals and reagents used were analytical grade and used without further purification. A stock solution of strontium was prepared by dissolving an appropriate amount of Strontium chloride hexahydrate ($\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$) (Merck) in distilled deionized water. The pH of each solution was adjusted to the required value with diluted nitric acid (HNO_3) and sodium hydroxide (NaOH) solutions.

Instrumentation: Sr concentrations in aqueous solution were determined by inductively coupled plasma optical emission spectrometry (ICP-OES). The adsorption experiments have been realized by batch technique using a thermostated shaker bath Model GFL-1083. The pH of the solutions was measured with a Hanna Instrument 8521 Model pH meter. A Hettich Zentrifugen Rotofix 32 Model digital centrifuge was used to centrifuge the samples. An oven (Electro-Mag M420 Model) and high temperature furnace (Carbolite Furnaces CSF-1100) were used to dry and calcine the samples, respectively.

Sorbents and preparing methods

Preparation of eggshell (ES): Eggshells were collected from local market of Turkey in 2013 and washed thoroughly in tap water first then in distilled water. The adhered membrane of eggshell was separated manually and eggshells dried at room temperature (30°C). The shells were later ground using a laboratory milling set, sieved to a particle size of below 125 µm and calcinated in an air at 850°C for 8 h. The thermal treatment was in two phases: In the first 30 min: Most of the organic materials were burnt out and the transformation of eggshell into calcium oxide (CaO) was obtained in the second phase²⁰.

Preparation of bone ash (BA-HAP): Leg bones of the chicken were collected local market of Turkey in 2013 and cut into small pieces which were then kept in ether for 2 days to remove fat from bone and placed in distilled water. The bone fraction was washed thoroughly with deionized-distilled water and dried at 105°C for 2 h. The bone was ground and sieved

to obtain particle size of below 125 μm. Then the bone pieces were ignited at 300°C and ashed at 850°C for about 8 h. The treatment enabled organic matter present in the bone to get volatilized, resulting in bone ash. The BA-HAp was stored in polythene containers at room temperature until to be used later.

Characterization of adsorbents: The resulting sorbents were characterized by X-ray diffraction (XRD), Rigaku (D/MAX-2200/PC), scanning electron microscopy (SEM, JEOL JSM-6060) and Fourier-transform infrared spectroscopy (FT-IR, Perkin Elmer BX2).

Determination of pH_{pzc} : The point zero charge (pH_{pzc}) of the adsorbents was determined using the following procedure: 20.0 mL of 0.10 mol L⁻¹ potassium nitrate (KNO₃) solution was placed in a closed capped Erlenmeyer flask. Initial pH values ($pH_{initial}$) of KNO₃ solutions were adjusted from ~4.0 to ~11.0 by addition of 0.1 M HNO₃ or KOH²¹. Suspensions of ES and BA-HAP were allowed to equilibrate for 24 h in a shaker thermostated at 25°C. Then the suspensions were filtered through a Whatman filter paper no: 44 and the pH values (pH_{final}) were measured again. Then the pH_{pzc} is the point where the curve of pH_{final} (pH_f) versus $pH_{initial}$ (pH_i) crosses the line and equals to pH_{final} .

Batch adsorption experiments: All adsorption experiments were performed by the batch technique using 10 mg of sorbents suspended in 10 mL of strontium solution in a polyethylene (PE) flask at selected pH. The flasks were shaken at different temperatures and contact times. The parameters such as contact time, pH, Sr(II) concentration, liquid/mass (V/m) ratio and temperature on the adsorption of Sr(II) was determined by changing a parameter and keeping others constant.

The supernatants were separated from the solids by centrifugation for 5 min at 4000 rpm. Concentration of Sr(II) in aqueous solution was determined by Perkin Elmer Optima 2000 DV ICP-OES. The amount of adsorbed Sr(II) ions was calculated from the difference in the Sr(II) concentration in aqueous solution before and after adsorption. The results were given as the adsorption capacity of Sr(II) ions sorbed per gram sorbent (q_e , mg g⁻¹), which was calculated by the following:

$$q_e = \frac{(C_i - C_e)}{W} [=] \frac{mg}{g} \quad (1)$$

where, C_i and C_e are the initial and equilibrium concentrations of Sr (mg L⁻¹) in solutions, respectively, W the weight of the sorbent (g) and V the volume of the aqueous phase (L). The blank experiments found adsorption of Sr on the walls of the flask to be negligible. The concentration of matrix metal ions in the solution was also measured by ICP-OES. All the experiments were performed in duplicates whose experimental errors were lower than ±3%.

Artificial neural network modelling: It should be mentioned that it is sufficient for most applications of artificial neural networks (ANNs) in engineering practice to use such a simple network structure (Fig. 1). Apart from the real input quantity, the independent variable x , there is a second input in most practically used implementations of ANN algorithms which is assumed to be constant $x_2 = 1.0$. This so-called bias variable is a technical measure to improve the learning capability of the network. Each node j in the hidden layer receives the output signals of all nodes k in the input layer. From these signals a weighted average is formed within each node j . Let w_{kj} be the weight, which is associated to the input signal, which the j -th node of the hidden layer receives from the k -th input node. The algorithm most often applied in practice is the famous

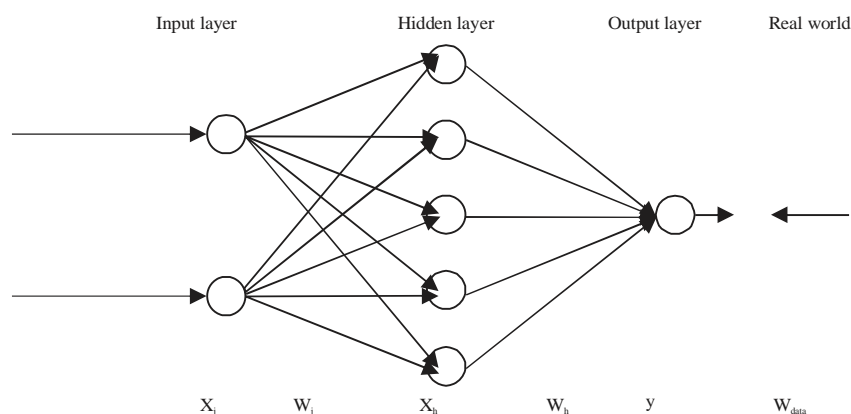


Fig. 1: Artificial neural network architecture

error backpropagation technique: Its philosophy is learning from examples, provided as (x_{data}, y_{data}) -pairs from the concrete process to be described by the network. We start with arbitrarily chosen elements in the weight vectors/matrices w_i and w_h . The first action is to determine the error, $Err (= y_{data} - y)$, between the network output y upon an arbitrarily but fixed input vector $x = [x_{data} \ 1]$ and the corresponding value (target) y_{data} from the training data set. In order to minimize the error, we make use of the least square criterion²²:

$$K = (y_{data} - y)^2 \rightarrow \min \quad (2)$$

In this study it was used a simple algorithm error backpropagation technique coding by MATLAB 7 software for the comparison of the removal efficiencies of Sr(II).

Determination of adsorption isotherms: The adsorption equilibrium data of strontium onto ES and BA-Hap was analyzed in terms of Freundlich, Langmuir and D-R isotherm models. The conditions of the experiment were as followings: ES, pH:6, m: 0.01 g, v: 10 mL, T: 25 °C, t: 120 min, (b) BA-HAP, pH: 5, m: 0.01 g, v: 10 mL, T: 25 °C, t: 180 min.

RESULTS AND DISCUSSION

Identification and characterization

FT-IR: The FT-IR spectra of ES and BA-HAP are shown in Fig. 2a and b, respectively. The FT-IR spectrum (Fig. 2a) of ES illustrates the peak at 551 cm^{-1} corresponding to CaO and 3640 cm^{-1} stretching mode of OH groups. These peaks confirm the presence of CaO and Ca(OH)_2 and the small

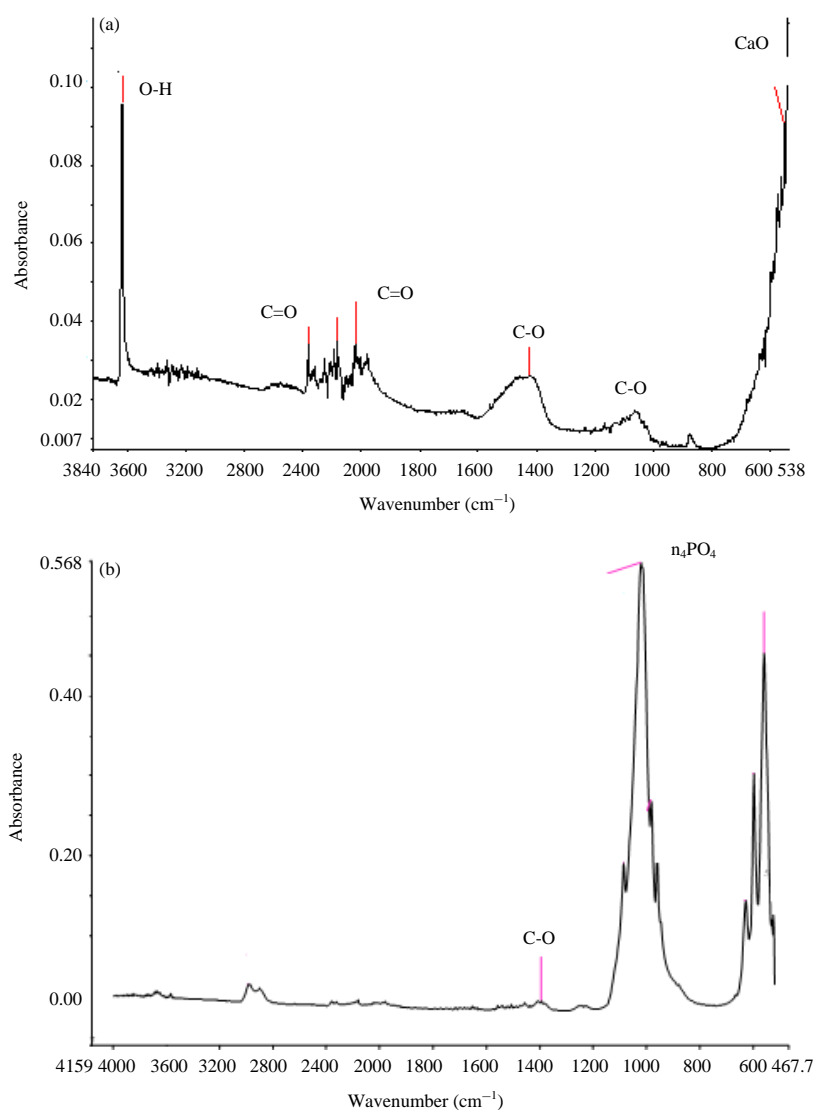


Fig. 2(a-b): FTIR spectrum of the (a) ES and (b) BA-HAP

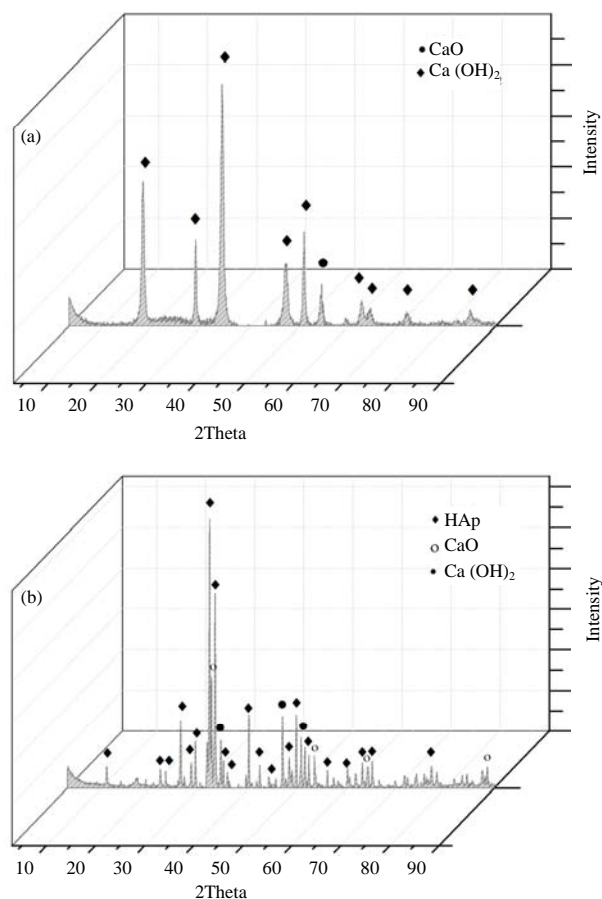


Fig. 3(a-b): XRD pattern of the (a) ES and (b) Ba-HAp

amount of CaCO_3 in the samples, respectively²³. The peaks in the spectrum between 2040 and 2358 cm^{-1} represent stretching mode of C=O groups, C-O stretching peak is at 1424 cm^{-1} and C-O bending peak is at 1062 cm^{-1} .

The FT-IR spectrum of BA-HAp shows peaks at $961\sim 1021$ and $560\sim 598\text{ cm}^{-1}$ representing the typically well crystallized apatite phase. The peak at 961 cm^{-1} corresponds to ν_1 stretching mode and that at 1021 cm^{-1} represents ν_3 vibration mode of phosphate groups. The sharp peaks at $569\sim 598\text{ cm}^{-1}$ are assigned to the bending mode of phosphate. The band at 1394 cm^{-1} is due to the vibration mode of C-O groups. As mention in the literature, the spectrum is dominated by components of the triplet of n_4PO_4 bending mode at 599 and 560 cm^{-1} ²⁰.

XRD: The X-ray diffractograms of the powder samples (ES and BA-HAp) are presented in Fig. 3a and b. Figure 3a shows that ES sample represents characteristic diffraction peaks of CaO at only $2\theta = 53.8^\circ$. Calcium hydroxide was also observed at $2\theta = 18.1^\circ, 28.6^\circ, 34.1^\circ, 47.1^\circ, 50.7^\circ, 62.5^\circ, 64.2^\circ, 71.7^\circ$ ve 84.7° . Figure 3b illustrates the diffractogram of

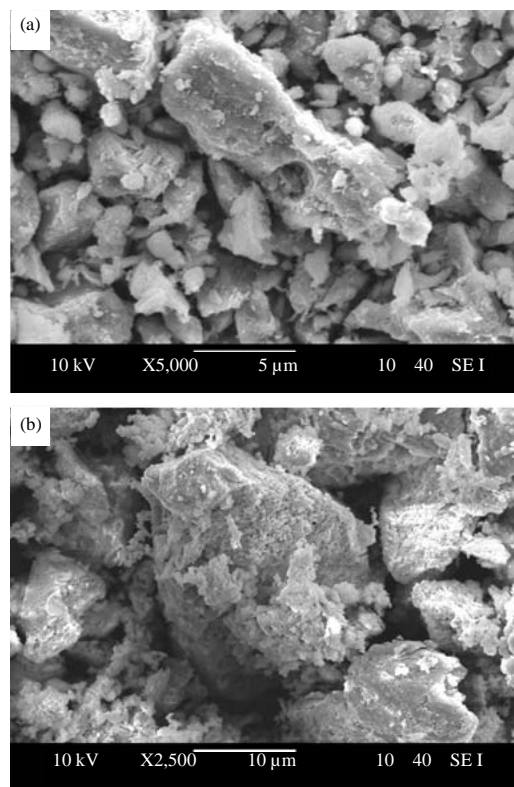


Fig. 4(a-b): SEM image of (a) ES (a) and (b) BA-HAp

BA-HAp. The peaks at 2θ values of $11.0, 21.8, 23.1, 28.21, 29.1, 31.9, 33.1, 34.8, 39.3, 39.9, 42.1, 45.4, 48.2, 49.6, 52.2, 56.1, 60.1, 61.8$ and 74.1° are quite identical to characteristic peaks of the HAp crystal which is in good agreement with the value JCPDS-PDF 74-0565 standard for calcium hydroxyapatite in crystalline phase²⁴.

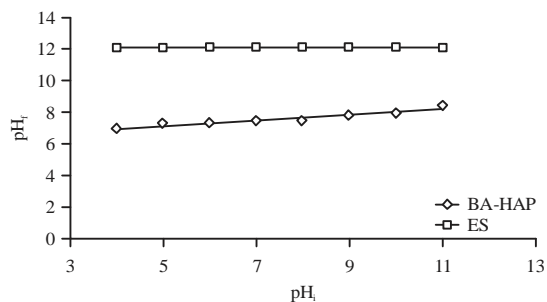
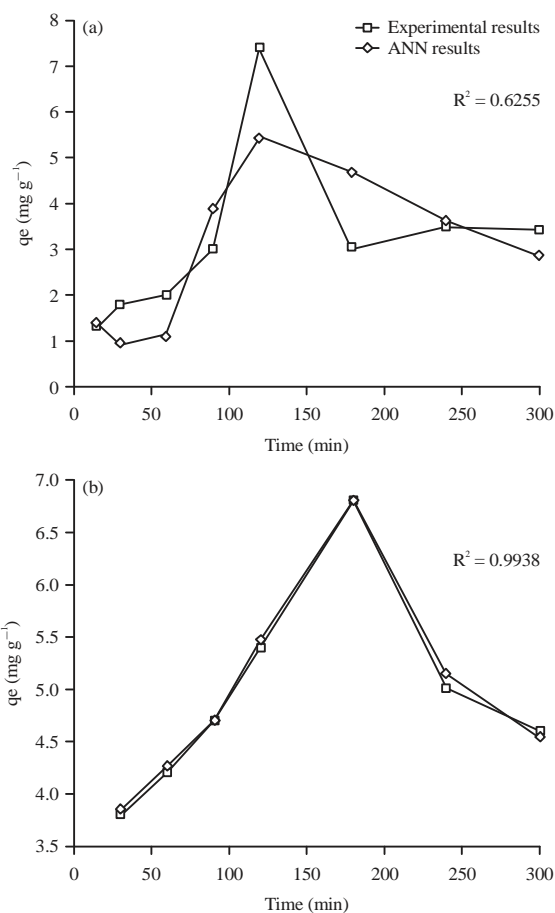
SEM: The SEM evidently revealed the surface texture and morphology of the sorbent materials at different magnifications. The SEM images of the surface of ES and BA-HAp are shown in Fig. 4 (5000x and 2500x magnification).

According to the Fig. 4a, ES powder has irregular shape of particles. The SEM images Fig. 4b also demonstrated hexagonal, homogeneous and regular apatite structure in the sample of BA-HAp.

pH_{pzc}: The point zero charge (pH_{pzc}) of the ES and BA-HAp determined by pH measurement technique was 11.60 and 7.66, respectively (Fig. 5).

Experimental parameters of Sr(II) adsorption

Effect of contact time: The effect of contact time on adsorption of Sr(II) onto ES and BA-HAp was studied for a shaking time of 15-300 min (Fig. 6). The change in the rate of

Fig. 5: Point of zero charge (pH_{pzc}) of ES and BA-HAPFig. 6(a-b): Agreement between ANN outputs and experimental data as a function of contact time for (a) ES and (b) BA-HAP (for ES and BA-HAP, c: 25 mg L⁻¹, m: 0.01 g, v: 10 mL, T: 25 °C)

adsorption might be caused by the fact that initially all sorbent sites were available and the solute concentration gradient was high. Furthermore, the less number of sorption sites, the much less adsorption rate by the sorbent, which shows the possible monolayer formation of Sr(II) ion on the outer surface, especially by the end of the experiments.

About 120 min was thus selected for ES and 180 min selected for BA-HAP in all subsequent experiments.

Figure 6 shows a comparison between the ANN model predictions and the experimental data as a function of contact time. It can be seen that the ANN model for BA-HAP sufficiently predicts the trend of the experimental data more than ES.

Effect of pH: The pH of the solution is a significant factor which controls sorption process based on ionization of surface functional groups and change of the solution composition. Sorption of Sr on the adsorbents was studied using the initial pH ranging from 2-10 and 2-9 for ES and BA-HAP, respectively. The effect of pH on the adsorption of Sr(II) ions onto the two kinds of adsorbents is shown in Fig. 7. Maximum adsorption values were observed at pH 6 for ES and at pH 5 for BA-HAP.

When pH is low (pH 2-3), the adsorbents almost have no more affinity to Sr(II) ions. Therefore, H⁺ ions replaces with Sr(II) ions that adsorbed to the adsorbents. As a result of this, adsorption capacity of Sr(II) ions decreases. When pH values increase beyond 6.0, precipitation starts due to the formation of complexes in the aqueous solution and then the adsorption decreases²⁵⁻²⁷.

In addition the point zero charge (pH_{pzc}) of ES and BA-HAP could be used to explain this influence. In this study the pH_{pzc} of ES and BA-HAP were found 11.60 and 7.66, respectively. So, at pH values lower than 11.60 and 7.66 ($\text{pH} < \text{pH}_{\text{pzc}}$) the surface of the adsorbents was positively charged, inhibiting the adsorption of Sr(II) ions due to the electrostatic repulsion between cationic structure of strontium and adsorbents. On the other hand, at pH values above 11.60 and 7.66 ($\text{pH} > \text{pH}_{\text{pzc}}$) the surface of the adsorbents was negatively charged, facilitating the electrostatic attraction between the strontium ions and this phenomenon causes the increasing the Sr(II) removal percentage. Based on the above mentioned reasons, the optimum pH of ES and BA-Hap was selected as 6 and 5, respectively.

The agreement between the ANN model predictions and the experimental data as a function of initial pH is shown in Fig. 7. From this plots it can be seen that obtained results from the proposed ANN model for ES and BA-HAP are in good agreement with the experimental data.

Effect of Sr concentration on the equilibrium adsorption amount:

In this study, the effect of initial Sr ion concentration was studied in the range of 10-50 mg L⁻¹ (Fig. 8). It is clear from the Fig. 8, the adsorption capacity of the adsorbents for

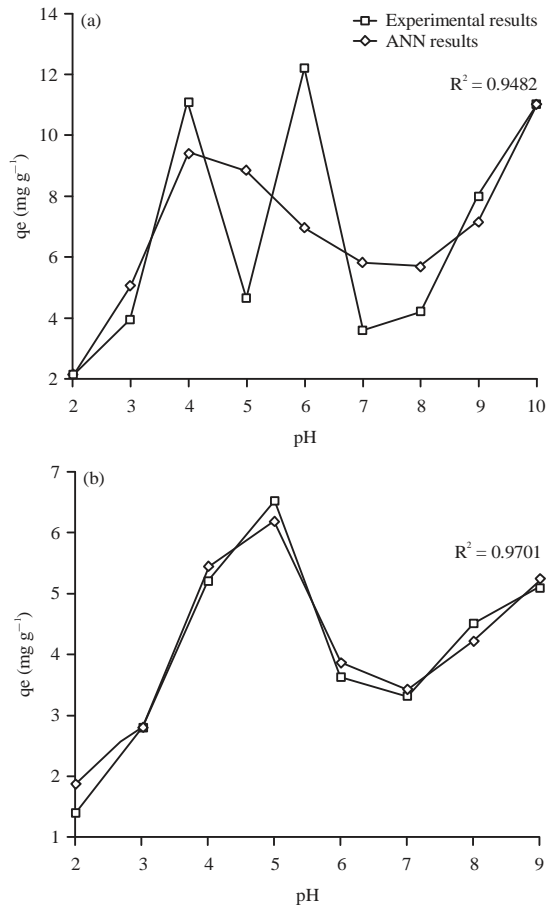


Fig. 7(a-b): Agreement between ANN outputs and experimental data as a function of pH for (a) ES and (b) BA-HAP. (a) ES, c: 25 mg L⁻¹, m: 0.01 g, v: 10 mL, T: 25°C, t: 120 min, (b) BA-HAP, c: 25 mg L⁻¹, m: 0.01 g, v: 10 mL, T: 25°C, t: 180 min)

Sr(II) ions increases due to the elevations of initial strontium concentration. The increase in the uptake capacity of the adsorbents (ES and BA-HAP) with increasing initial ion concentration may be accounted for by higher likelihood of collision between ions and the calcium-based adsorbents and by higher concentration gradient which increases mass transfer rate²⁸. Therefore, 25 mg L⁻¹ Sr (II) concentration was selected for further experiments with all the sorbents. The experimental data and ANN calculated outputs for various initial Sr(II) ions concentration values are shown in Fig. 8. It can be seen that the ANN model shows a good performance on prediction of the experimental data.

Effect of V/m ratio: The effect of volume/mass (V/m) ratio on the adsorption of Sr(II) ions was studied using constant sorbent dosage and different volume in the range of 500-2500

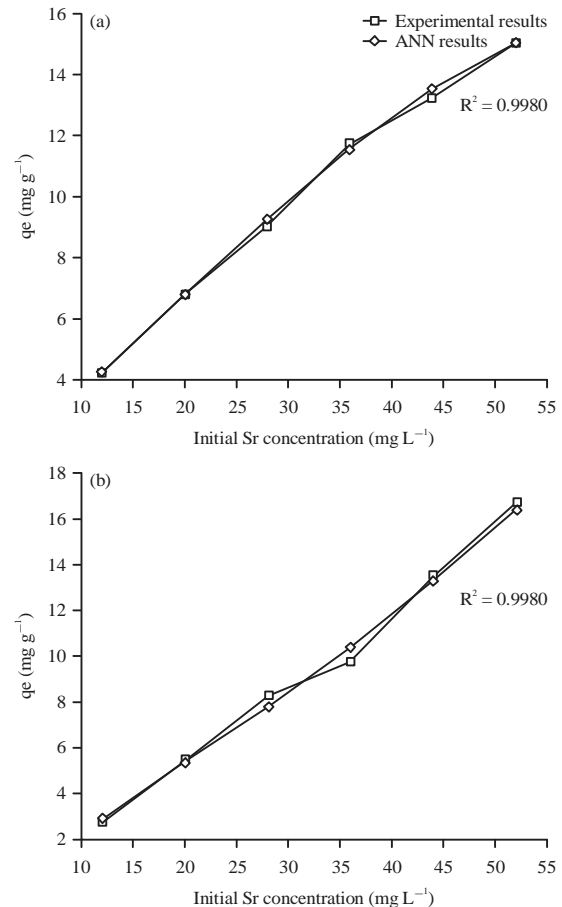


Fig. 8(a-b): Agreement between ANN outputs and experimental data as a function of initial strontium concentration (a) ES, pH:6, m: 0.01 g, v: 10 mL, T: 25°C, t: 120 min, (b) BA-HAP, pH: 5, m:0.01 g, v: 10 mL, T: 25°C, t: 180 min)

(Fig. 9) and the optimum adsorbent weight evaluated to achieve a high removal capability. Figure 9 shows the effect of V/m ratio on the adsorption process. The adsorption capacity (q_e) increases as V/m ratio decreases from 2500-500. The results indicated that the adsorption efficiency is dependent on the volume of the solution. Adsorption rate of the strontium ions decreased with the liquid volume increasing.

This trend could be explained by the fact that a dilution of the sorbents appeared at higher volume of the solution at constant adsorbents and resulted in a decrease in contact for solute and adsorbent in the solution. The V/m was kept at 1000 during all the experiments for further experiments with all sorbents.

Effect of temperature: Temperature is a highly significant parameter which governs the adsorption process. The effect of temperature on Sr(II) adsorption by ES and BA-HAP was

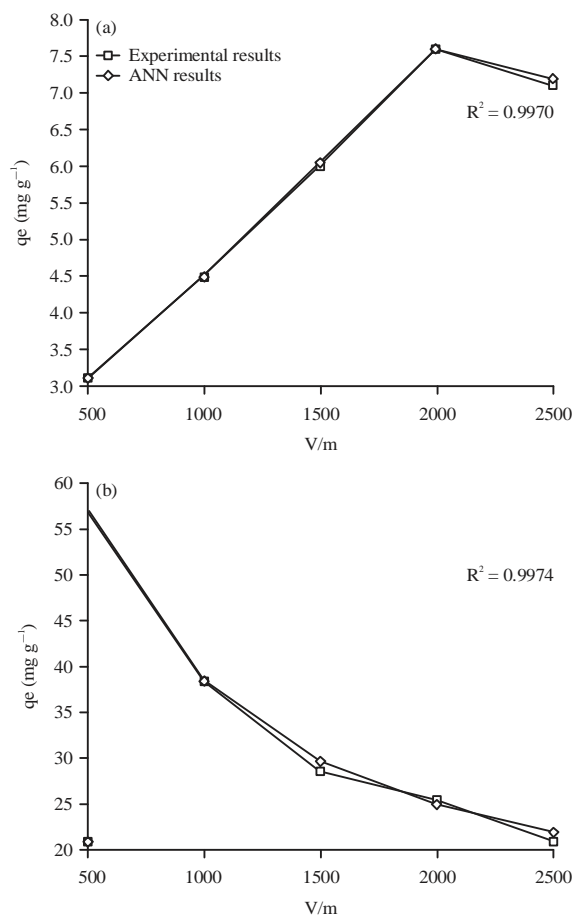


Fig. 9(a-b): Agreement between ANN outputs and experimental data as a function of V/m ratio (a) ES, c: 25 mg L⁻¹, pH: 6, m: 0.01 g, v: 10 mL, T: 25°C, t: 120 min and (b) BA-HAP, c: 25 mg L⁻¹, pH: 5, m: 0.01 g, v: 10 mL, T: 25°C, t: 180 min)

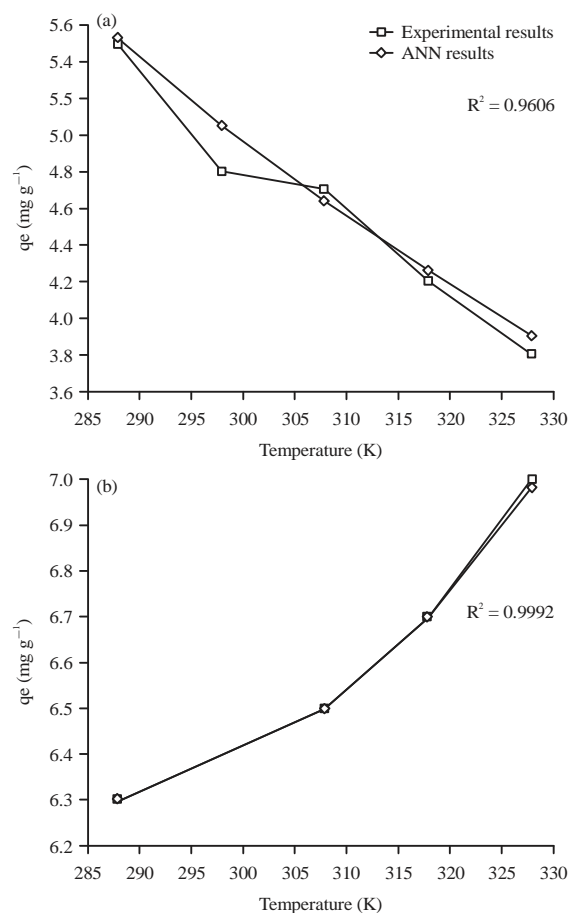


Fig. 10(a-b): Agreement between ANN outputs and experimental data as a function of temperature (a) ES, c: 25 mg L⁻¹, pH: 6, m: 0.01 g, v: 10 mL, T: 25°C, t: 120 min and (b) BA-HAP; c: 25 mg L⁻¹, pH: 5, m: 0.01 g, v: 10 mL, T: 25°C, t: 180 min)

therefore, investigated (Fig. 10). The figure illustrates that the percent removal of Sr(II) decreased with increased temperature for ES. The decrease in Sr(II) removal with increase in temperature could be due to physical bonds weakening between the Sr ions and the active site of the adsorbents and this observed trend also suggests that the adsorption of Sr(II) by ES is kinetically controlled by an exothermic process. However, the percentage of sorption of BA-HAP was slightly increased with a rise of temperature. The conclusion from the BA-HAP revealed the endothermic nature of the adsorption.

Adsorption isotherms: The values of correlation regression coefficient (R^2) obtained from the Freundlich isotherm model (0.992 and 0.996 for ES and BA-HAP, respectively) are higher than those of the Langmuir isotherm model (0.94 only for

BA-Hap), which suggests that the Freundlich isotherm model is more suitable to explain the experimental data (Fig. 11, Table 1).

The D-R isotherm model well fitted the equilibrium data for the adsorbents since the R^2 values were found to be 0.993 and 0.998 for Sr(II) adsorption on ES and BA-Hap, respectively (Fig. 12, Table 1). In addition, the mean energy of adsorption (E) was calculated as 0.61 and 0.75 kJ mol⁻¹ for ES and BA-Hap, respectively. From the results it can be concluded that Sr adsorption on the sorbents are predominantly performed by physical adsorption.

Thermodynamics studies: The thermodynamic parameters for the adsorption process were calculated by the following equations:

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (3)$$

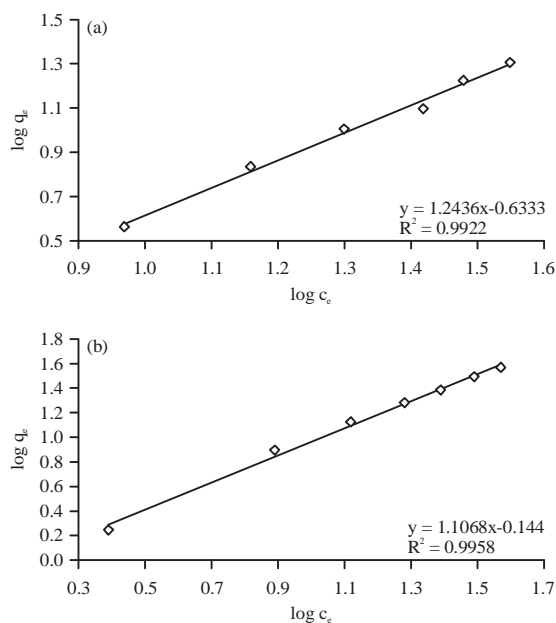


Fig. 11(a-b): Freundlich isotherm plots for the sorption of Sr(II) ions on (a) ES and (b) BA-HAp

Table 1: Adsorption isotherm constants for the adsorption of Sr on ES and BA-HAp

Isotherm models	Parameters	ES	BA-Hap
Langmuir	Q_0 (mg g ⁻¹)	40.983	66.225
	b_L (L mg ⁻¹)	0.009	0.010
	R^2	0.765	0.943
	R_L	0.811	0.959
Freundlich	K_f (mg g ⁻¹)	0.232	0.717
	$1/n_f$	1.243	1.107
	R^2	0.992	0.996
Dubinin-Radushkevich	X_m (mg g ⁻¹)	$2.6H10^{-2}$	6.31×10^{-3}
	E (kJ mol ⁻¹)	0.61	0.75
	R^2	0.993	0.998

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (4)$$

where, K_d is the distribution coefficient (mL g⁻¹), S° is standard entropy (kJ mol⁻¹), H° is standard enthalpy (kJ mol⁻¹), T is the absolute temperature (K) and R is the gas constant (8.314 J mol⁻¹ K). The experiments were conducted at 288, 298, 308, 318 and 328 K. The values of ΔH° and ΔS° were determined from the slopes and intercepts of the plots of $\ln K_d$ vs. $1/T$ (Fig. 13) for the adsorbents. ΔG° was also calculated using Eq. 4. The values of the thermodynamic parameters for the adsorption of Sr(II) on ES and BA-HAp are illustrated in Table 2.

The positive value of H° for the processes for BA-HAp further confirms the endothermic nature of the process. Nevertheless, the negative value of H° for the processes with ES also confirms the exothermic nature of the process. When the value of ΔH° is lower than 40 kJ mol⁻¹, it can be conclude that the adsorption process is physical. Obtained ΔH° values

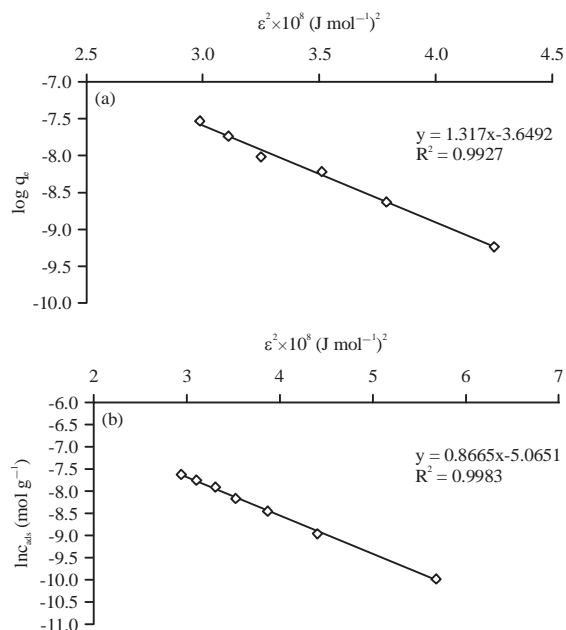


Fig. 12(a-b): D-R isotherm plots for the sorption of Sr(II) with (a) ES and (b) BA-HAp

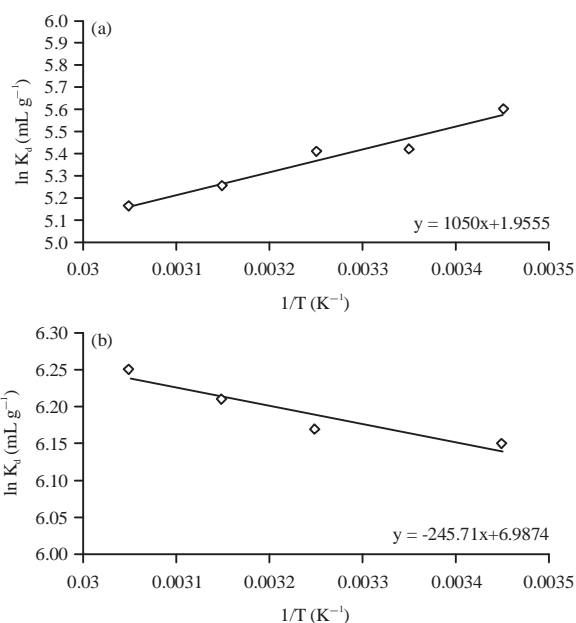


Fig. 13(a-b): Plots of $\ln K_d$ versus $1/T$ for Sr adsorption on (a) ES and (b) BA-HAp

are -8.72 and 2.04 kJ mol⁻¹ for ES and BA-HAp, respectively and indicate that the adsorption process has physical nature with weak Vanderwaals forces of attraction²⁹, which is consistent with the results of the isotherm models. The positive value of S° reflects the affinity of the adsorbent material toward Sr and the negative values of G° show that the adsorption process is spontaneous and more favourable at higher temperatures³⁰.

Table 2: Thermodynamic parameters of Sr adsorption on ES and BA-HAp

Sorbent	ΔH° (kJ mol ⁻¹)	ΔS° (kJ mol ⁻¹)	ΔG° (kJ mol ⁻¹)				
			288k	298k	308k	318k	328k
ES	-8.72	0.016	-13.33	-13.49	-13.65	-13.81	-13.97
BA-Hap	2.04	0.058	-14.66	-15.24	-15.82	-16.40	-16.98

CONCLUSION

The natural calcium based adsorbents seems to be a suitable low-cost material for removing strontium ions from aqueous solutions. The pH experiments showed that sorption is relatively high at pH 5 for BA-HAp and pH 6 for ES. From ANN modelling results it is evident that ANN model is an effective technique in modeling, estimation and prediction of adsorption process. Moreover, the ANN model could be used for performing the analysis of nonlinear interactions of input variables on adsorption parameters. It also provides idea for disposal of waste solutions including strontium. The evidence of our laboratory-scale studies could be applicable in the process of industrial wastewaters adsorption.

SIGNIFICANCE STATEMENTS

This study discovers that eggshell powder (ES) and natural hydroxyapatite (HAp) derived from chicken bone could effectively remove strontium ions. Also, the artificial neural networks (ANN) are carried out for prediction of adsorption efficiency for the removal of Sr(II) ions from aqueous solution by eggshell (ES) and bone ash-hydroxyapatite (BA-HAp). The results of this study help the researchers to use natural calcium based adsorbents because these type of adsorbents are economical, environment-friendly, efficient and convenient adsorbents for Sr(II) ion and the other pollutants from water and wastewater.

ACKNOWLEDGMENT

This master level research project was supported by Ege University Scientific Research Project Unit Project No. 2012 NBE 005.

REFERENCES

- Park, Y., Y.C. Lee, W.S. Shin and S.J. Choi, 2010. Removal of cobalt, strontium and cesium from radioactive laundry wastewater by ammonium molybdophosphate-polyacrylonitrile (AMP-PAN). Chem. Eng. J., 162: 685-695.
- Ghaemi, A., M. Torab-Mostaedi and M. Ghannadi-Maragheh, 2011. Characterizations of strontium(II) and barium(II) adsorption from aqueous solutions using dolomite powder. J. Hazard. Mater., 190: 916-921.
- Wu, L., J. Cao, Z. Wu, J. Zhang and Z. Yang, 2017. The mechanism of radioactive strontium removal from simulated radioactive wastewater via a coprecipitation microfiltration process. J. Radioanal. Nucl. Chem., 314: 1973-1981.
- Moon, J.K., K.W. Kim, C.H. Jung, Y.G. Shul and E.H. Lee, 2000. Preparation of organic-inorganic composite adsorbent beads for removal of radionuclides and heavy metal ions. J. Radioanal. Nucl. Chem., 246: 299-307.
- Sahai, N., S.A. Carroll, S. Roberts and P.A. O'Day, 2000. X-ray absorption spectroscopy of strontium(II) coordination: II. Sorption and precipitation at kaolinite, amorphous silica and goethite surfaces. J. Colloid Interface Sci., 222: 198-212.
- Tan, Y., J. Feng, L. Qiu, Z. Zhao, X. Zhang and H. Zhang, 2017. The adsorption of Sr(II) and Cs(I) ions by irradiated *Saccharomyces cerevisiae*. J. Radioanal. Nucl. Chem., 314: 2271-2280.
- Kim, G., K. Sim, S. Kim, S. Komarneni and Y. Cho, 2018. Selective sorption of strontium using two different types of nanostructured manganese oxides. J. Porous Mater., 25: 321-328.
- Cole, T., G. Bidoglio, M. Soupioni, M. O'Gorman and N. Gibson, 2000. Diffusion mechanisms of multiple strontium species in clay. Geochim. Cosmochim. Acta, 64: 385-396.
- Shawabkeh, R.A., D.A. Rockstraw and R.K. Bhada, 2002. Copper and strontium adsorption by a novel carbon material manufactured from pecan shells. Carbon, 40: 781-786.
- Esfandian, H., A. Akrami and F.B. Shahri, 2017. Application of Response Surface Methodology (RSM) for optimization of strontium sorption by synthetic PPy/perlite nanocomposite. Desalin. Water Treat., 93: 74-82.
- Kavitha, B. and D.S. Thambavani, 2016. Kinetics, equilibrium isotherm and neural network modeling studies for the sorption of hexavalent chromium from aqueous solution by quartz/feldspar/wollastonite. RSC Adv., 6: 5837-5847.
- Esfandian, H., A. Samadi-Maybodi, M. Parvini and B. Khoshandam, 2016. Development of a novel method for the removal of diazinon pesticide from aqueous solution and modeling by Artificial Neural Networks (ANN). J. Ind. Eng. Chem., 35: 295-308.

13. Asl, S.M.H., M. Ahmadi, M. Ghiasvand, A. Tardast and R. Katal, 2013. Artificial Neural Network (ANN) approach for modeling of Cr(VI) adsorption from aqueous solution by zeolite prepared from raw fly ash (ZFA). *J. Ind. Eng. Chem.*, 19: 1044-1055.
14. Mendoza-Castillo, D.I., N. Villalobos-Ortega, A. Bonilla-Petriciolet and J.C. Tapia-Picazo, 2015. Neural network modeling of heavy metal sorption on lignocellulosic biomasses: Effect of metallic ion properties and sorbent characteristics. *Ind. Eng. Chem. Res.*, 54: 443-453.
15. Kooh, M.R.R., M.K. Dahri, L.B.L. Lim, L.H. Lim and O.A. Malik, 2016. Batch adsorption studies of the removal of methyl violet 2B by soya bean waste: Isotherm, kinetics and artificial neural network modelling. *Environ. Earth Sci.*, 75: 783-797.
16. Yetilmmezsoy, K. and S. Demirel, 2008. Artificial Neural Network (ANN) approach for modeling of Pb(II) adsorption from aqueous solution by Antep pistachio (*Pistacia vera* L.) shells. *J. Hazard. Mater.*, 153: 1288-1300.
17. Prakash, N., S.A. Manikandan, L. Govindarajan and V. Vijayagopal, 2008. Prediction of biosorption efficiency for the removal of copper(II) using artificial neural networks. *J. Hazard. Mater.*, 152: 1268-1275.
18. Dimovic, S., I. Smiciklas, I. Plecas and D. Antonovic, 2009. Kinetic study of Sr²⁺ sorption by bone char. *Sep. Sci. Technol.*, 44: 645-667.
19. Metwally, S.S., H.E. Rizk and M.S. Gasser, 2017. Biosorption of strontium ions from aqueous solution using modified eggshell materials. *Radiochim. Acta*, 105: 1021-1031.
20. Krithiga, G. and T.P. Sastry, 2011. Preparation and characterization of a novel bone graft composite containing bone ash and egg shell powder. *Bull. Mater. Sci.*, 34: 177-181.
21. Smiciklas, I.D., S.K. Milonjic, P. Pfenndt and S. Raicevic, 2000. The point of zero charge and sorption of cadmium (II) and strontium (II) ions on synthetic hydroxyapatite. *Sep. Purif. Technol.*, 18: 185-194.
22. Lubbert, A., R. Simutis, N. Volk and V. Galvanauskas, 2000. Hands on course on biochemical process optimization and control. Martin Luther University, Germany.
23. Witoon, T., 2011. Characterization of calcium oxide derived from waste eggshell and its application as CO₂ sorbent. *Ceramics Int.*, 37: 3291-3298.
24. Slosarczyk, A., Z. Paszkiewicz and C. Paluszkiwicz, 2005. FTIR and XRD evaluation of carbonated hydroxyapatite powders synthesized by wet methods. *J. Mol. Struct.*, 744-747: 657-661.
25. Chen, C., J. Hu, D. Shao, J. Li and X. Wang, 2009. Adsorption behavior of multiwall carbon nanotube/iron oxide magnetic composites for Ni(II) and Sr(II). *J. Hazard. Mater.*, 164: 923-928.
26. Yusan, S. and S. Erenturk, 2011. Adsorption characterization of strontium on PAN/zeolite composite adsorbent. *World J. Nuclear Sci. Technol.*, 1: 6-12.
27. Liao, D., W. Zheng, X. Li, Q. Yang, X. Yue, L. Guo and G. Zeng, 2010. Removal of lead(II) from aqueous solutions using carbonate hydroxyapatite extracted from eggshell waste. *J. Hazard. Mater.*, 177: 126-130.
28. Li, Q., H. Liu, T. Liu, M. Guo, B. Qing, X. Ye and Z. Wu, 2010. Strontium and calcium ion adsorption by molecularly imprinted hybrid gel. *Chem. Eng. J.*, 157: 401-407.
29. De Luna, M.D.G., C.M. Futralan, C.A. Jurado, J.I. Colades and M.W. Wan, 2018. Removal of ammonium nitrogen from aqueous solution using chitosan coated bentonite: Mechanism and effect of operating parameters. *J. Applied Polym. Sci.*, Vol. 135. 10.1002/app.45924.
30. Gok, C., U. Gerstmann and S. Aytas, 2013. Biosorption of radiostrontium by alginate beads: Application of isotherm models and thermodynamic studies. *J. Radioanal. Nucl. Chem.*, 295: 777-788.