Journal of
Applied Research in Water and Wastewater
Journal homepage: www.arww.razi.ac.ir

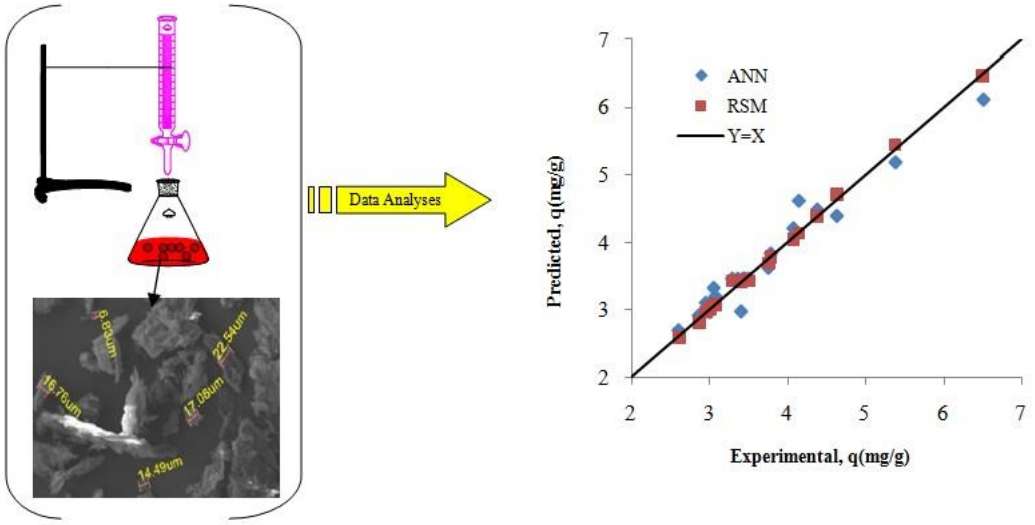
Original paper

Modeling and optimization study by response surface methodology on magnesium ions removal from hard water through a biosorbent

Abedin Raziani, Akbar Mohammadidoust*

Department of Chemical Engineering, Kermanshah Branch, Islamic Azad University, Kermanshah, Iran.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 15 February 2020
Reviewed 15 May 2020
Received in revised form 11 June 2020
Accepted 14 June 2020

Keywords:
Hard water
Response surface methodology (RSM)
Optimization
Biosorbent
Magnesium ions removal

ABSTRACT

Hazelnut shell was used as a green adsorbent and environment-friendly for magnesium ions (Mg^{2+}) adsorption from hard water solution in batch system. The characterization of the biosorbent was entirely evaluated using SEM, XRD and FT-IR analyses. Design of experiments (DOE) decreased the number of non-significant experiments, which resulted in reducing the time and cost of studies. Response surface methodology (RSM) was applied to dynamic assessment of the adsorption process. The effects of variables (pH, adsorbent dosage, Mg^{2+} concentration, time) and their interactions were investigated by central composite face design (CCFD). In addition, the numerical optimization was also analyzed. The results demonstrated that maximum efficiency, 56.21 %, and adsorbent capacity, 5.729 mg/g, occurred at initial concentration of 200 mg/L, adsorbent dosage of 1 g and pH 10 in duration of 59.816 min which were in good agreement with experimental results. In order to validate of the dynamic model, artificial neural network (ANN) was employed. Although RSM had a superior capability in developing of the model in comparison with ANN, it was acceptable to forecast the magnesium ions removal by both RSM and ANN approaches. Finally, the studies of the adsorption isotherms, kinetic models, reusability tests of the adsorbent and comparison with walnut shell were also done.

1. Introduction

Hardness of water has caused a serious problem in water resources and many industries, especially. Hard water heating can form the solid deposits of calcium carbonate. The sediments act as a resistance and have a negative effect on heat transfer. Moreover, it makes pressure drop and sometimes blockage of pipes. Therefore, it reduces equipment life and results in higher cost and lower productivity (Inspectorate. 1999; Tchobanoglous and Burton. 2003; Tyusenkov and Cherepashkin. 2014). The hardness is mainly determined by two

*Corresponding author Email: mohammadidoust@gmail.com

calcium and magnesium metals. In general, the categories of hard water are: 0 to 60 ppm as calcium carbonate is soft water, 61 to 120 ppm, moderate, 121 to 180 ppm, hard and more than 180 ppm is very hard (Tchobanoglous and Burton. 2003). Groundwater hardness can be created due to the presence of minerals in soil and rock. Although minerals are helpful for health, they must be controlled at a certain limit to prevent the diseases (Tchobanoglous and Burton. 2003). Among the several methods such as ion exchange, adsorption, electrochemical, chemical precipitation, membrane and etc., adsorption process is able in the uptake of the metals. Because it is safe, cost-effective and high quality (Eccles. 1999; Tchobanoglous and Burton. 2003). Metal ions adsorption has been studied by many researchers. Recently, the effect of nanobubbles on heavy metal ions adsorption was investigated. In that work, Lead ions were adsorbed through activated carbon which was made by pyrolysis potato peels. Although nanobubbles did not increase the adsorption capacity, they accelerated it by 366 % (Kyzas et al. 2019). In another research, biogenic iron compounds were used to remove copper, zinc, arsenate and chromate from aqueous solutions. Arsenic adsorption was in a higher level compared with the other metals (Castro et al. 2018). The hazelnut shell was employed for Zn (II) removal from leachate. In that work, Zn (II) concentration decreased by almost 12 % (Turan et al. 2011). In another study, to remove of Cd^{2+}, Zn^{2+} and Cr^{3+} from aqueous solution, hazelnut shell was also used. Cr^{3+} adsorption was more than both Cd^{2+}, Zn^{2+} in mixed solutions (Cimino et al. 2000). In recent years, black cumin and biochar were employed as a bioadsorbent to remove Pb (II) and Cd (II) (Bingol et al. 2012; Ni et al. 2019). Furthermore, activated carbon as a conventional sorbent was applied in many works (Aghav et al. 2011; Monser and Adhoum. 2002; Xu et al. 2008). Although different adsorbents have been used on the removal of heavy metals such as Cr (Babel and Kurniawan. 2004; Low et al. 1995; Ogata et al. 2018), As (Castro et al. 2018; Ogata et al. 2018), Zn (Esalah et al. 2000; Low et al. 1995; Monser and Adhoum. 2002; Turan et al. 2011; Wu et al. 2019), Cd (Al-Senani and Al-Fawzan. 2018; Esalah et al. 2000; Ngah and Hanafiah. 2008; Pedersen. 2003; Rostami and Joodaki. 2002; Wu et al. 2019; Zhang et al. 2010), Co (Ngah and Hanafiah. 2008), Pb (Ngah and Hanafiah. 2008; Pavan et al. 2008; Zhang et al. 2010), Cu (Cardoso et al. 2004; Hong et al. 2019; Marshal and Johns. 1996; Pamukoglu and Kargi. 2006), light metals has rarely been studied. In addition, magnesium removal by hazelnut shell from hard water solutions has not been investigated.

Developing the mathematical and statistical methods for analyzing data of the adsorption process is necessary. Design and analysis of experiments determine the number of significant experiments, model and optimization of process conditions. It is useful to decrease the number of experiments, cost and time of experiments (Montgomery. 2008). In the past, univariate mathematical method was mostly applied to analyze. It could not interpret the effects of independent variables and their interactions. Nowadays, multivariate mathematical and statistical methods make an excellent investigation of problems. Recently, response surface methodology (RSM) has attracted more attention as a powerful tool in analyzing the behavior of independent variables and their interactions. The RSM depicts the path of experiments, mathematics and statistics simultaneously (Montgomery. 2008). The performance of the biosorption process is mainly complex and nonlinear. Therefore, it can be reasonable to employ RSM by central composite face design (CCFD) and Box-Behnken design (BBD) methods. In CCFD and BBD, numerical and graphical optimizations specify the optimal conditions and best responses (Mohammadidoust et al. 2016a). In recent decay, RSM has been used as a capable methodology in the adsorption processes (Hasan et al. 2009; Preetha and Viruthagiri. 2007; Singh et al. 2010). Moreover artificial intelligence (AI) has been applied in the modeling and optimization of environmental processes, wastewater and contaminated solutions treatment, especially (Prakash et al. 2008; Saber et al. 2009). Artificial neural networks (ANNs) as one of the extremely useful of AI, is viable and promising approach in developing nonlinear behavior of complex processes. When the mathematical model fails to define of problem which contains different variables, numerical methods may be well estimation the corresponding model (Bingol et al. 2012; Turan et al. 2011). ANN attempts to solve problems by inspiring the biological structures such as the brain and nerves systems. It consists of three layers including input, hidden and output which neurons are linked to others of next layer. Finally, they produce an interconnected group through weights and biases (Mohammadidoust et al. 2015; Mohammadidoust et al. 2016b). Therefore, using the new methods, numerical and statistical, can play a crucial role in optimizing and modeling complicated processes. In recent years, applying both ANN and RSM methods has been very interesting to authors (Desai et al. 2008; Geyikci et al. 2012; Kasiri et al. 2008; Khayet et al. 2011; Ranjan et al. 2011; Shihani et al. 2006).

The main purpose of this work is assessment of the magnesium ions reduction of hard water using the hazelnut shell as low cost, easy available, environment-friendly and safe for human, in order to decrease sediments of equipment. To achieve this aim, the RSM was applied to select of experiments, optimize the factors and responses of the process, based on CCFD. Afterwards, a three-layer ANN model by feed-forward back propagation type relying on Levenberg-Marquardt algorithm was also trained. In addition, the attained results of the RSM and ANN models were compared and optimal conditions due to the numerical methods were determined. Finally, adsorption isotherms, kinetic models, reusability tests of the adsorbent and comparison with walnut shell were also evaluated.

2. Materials and methods

2.1. Materials

In order to the preparation of the stock solutions, $MgCl_2.6H_2O$ (M_w=203.295 g/mol) was used. The dilution process was implemented by deionized water to the desired initial concentrations. complexometric titration was performed to analyze of the magnesium ions amount with EDTA, E.C.B.T, calcium carbonate, hydrogen chloride (37 %), ammonia (25 %), ammonium chloride, murexide and sodium chloride. Al the chemicals were supplied from Merck, Inc.

2.2. The biosorbent preparation

Green hazelnuts were purchased from a local market in Kermanshah, Iran. First, hazelnut shells were separated and washed with deionized water several times to remove dust and air pollutants. To dry the hazelnut shells, they were kept in an oven at 45 °C for 48 h. The shells further crushed by simple and planetary bal mills. Then, the particles were sieved with a 52 mesh size screen (300 µm, openings). Table 1 shows the chemical characterizations of the hazelnut shells which used in this research.

Table 1. The chemical characterizations of the hazelnut shells.

Component	Value, %
Oxygen	44.18
Carbon	48.93
Hydrogen	5.38
Sulfur	0.50
Ash	1.01

2.3. Adsorption procedure and analyses

The experiments of Mg^{+2} removal were conducted using the hazelnut shells, in batch system with a volume of 100 ml. A certain weight (0.4-1 g) of the sorbent was introduced into beaker which contains 50 ml of Mg^{+2} solution (100-200 mg//L). The pH adjustments were obtained with a pH meter (Metrohm 827, Swiss) through 0.1 M HCl or 0.1 M NaOH. The top of the beaker was closed and placed on an analogue orbital shaker (GFL 3005, Germany) at rotation speed of 160 rpm and constant temperature of 25 ºC. After the known time intervals (20, 40 and 60 min), the sample was filtered and centrifuged. Then, the residual concentration of Mg^{+2} solution was analyzed by complexometric titration method. Al the experiments were carefully performed in duplicate, to attain an exact value due to average of the values.

The micro-structural study of the biosorbent was carried out using scanning electron microscopy (SEM, KYKY EM-3200, China). Moreover, X-Ray fluorescence spectrophotometer (XRF, PW 1480, Philips, Netherlands) was employed to determine the adsorbent compositions. To evaluate the biosorbent capability in the adsorption process, FT-IR (Thermo Nicolet, US) and XRD (STOE-STADI P, Germany) tests were also investigated. The efficiency of Mg^{2+} removal (R) and biosorbent capacity (q, mg/g) as the responses of the RSM were considered, which were calculated as follows:

$$R\,(\%) = \left(\frac{C_\circ - C}{C_\circ}\right) \times 100 \quad (1)$$

$$q = \left(\frac{C_\circ - C}{m}\right) \times V \quad (2)$$

Please cite this article as: A. Raziani, A. Mohammadidoust, Modeling and optimization study by response surface methodology on magnesium ions removal from hard water through a biosorbent, Journal of Applied Research in Water and Wastewater, 7 (1), 2020, 77-89.

where, C_0 and C are the initial and final concentrations of Mg^{2+} in solution (mg/l) respectively, m is the hazelnut shell dosage (g) and V is total solution volume (L).

3. Results and discussion

3.1. Biosorbent studies

The hazelnut shells consist of some elements which have been reported in Table 1. As seen in XRF analysis, carbon (48.93), oxygen (44.18) and hydrogen (5.38) have significant contents, respectively. Two pairs of free electrons in oxygen atom can be effective in the adsorption process between the surface of the sorbent and magnesium atom. In addition, hydrogen bonding with pH changes may constitute a force and attempt to adsorb magnesium ions species (Hasan et al., 2009). The micro-structures of the biosorbent are illustrated in Fig.1. Scanning electron microscopy (SEM) showed the surface structure at magnifications of 30, 50, 100 µm. It can be clarified that the particles were on a micro scale (6.38, 14.49, 16.76, 17.08 and 22.54 µm) as shown in Fig. 1c. Moreover, porous and irregular morphology of adsorbent led to improve the uptake of magnesium ions into different active sites. In the image on the 30 µm scale (Fig. 1 a), it indicates the adsorbent particles uniformly, but as the scale rises (50, 100 µm) as indicated in Fig. 1c and d, the aggregated components are more evident.

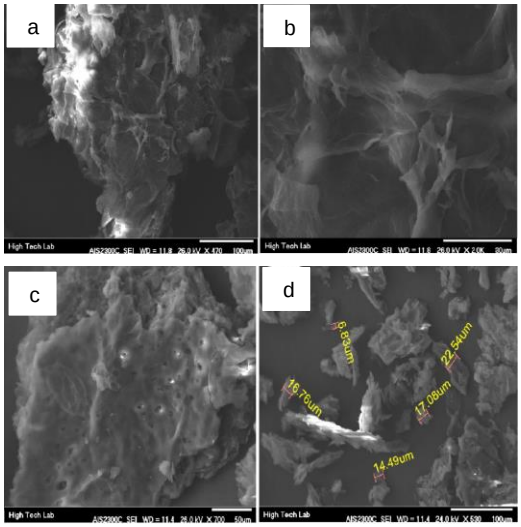


Fig. 1. Scanning electron microscopy (SEM) of hazelnut shells, (a) 30 µm, (b) 100 µm (× 470), (c) 100 µm (× 530), (d) 50 µm.

FT-IR spectra depicted the sorbent constituents in the region of 400-4000 cm^{-1}, before and after magnesium ions adsorption. As shown in Fig. 2, the peak in 1060 cm^{-1} related to the C-O stretching vibration. The C=C bond vibration frequency can be seen in 1618 cm^{-1}. Furthermore, the 2925 cm^{-1} band was assigned to the C-H stretching vibration in aliphatic. The peaks of 3416 cm^{-1} and 3424 cm^{-1} could verify the stretching vibration of –OH group. Thereby, hydrogen bonding was confirmed in the hazelnut shells. The influence of the magnesium ions on the –OH group was made that the –OH transferred to lower frequency (3424 to 3416 cm^{-1}) and then the bandwidth decreased. It was resulted in increasing the percentage of light passing (30% to 60%). Therefore, the 3416-3424 cm^{-1} bands may be attributed to the magnesium ions adsorption on the hazelnut shells. Fig. 3 demonstrated XRD pattern of the sorbent loaded with the magnesium ions. It can be realized broad peaks with high intensities. Maximum peak (011) was found at a 2θ of 38 degrees. According to the pattern, $Mg(OH)_2$ trigonal crystals was approved due to the JCPDS card no. 96-900-6331. Spreading peaks can also be a reason which the particles were small (microscale).

3.2. Design of experiments (DOE)

3.2.1. Response surface methodology (RSM)

In this work, Design Expert software (version 10.0.7) was employed. Factorial design and response surface methodology are two basic approaches in the design of experiments. The RSM assessments the effects of the independent variables; main, quadratic and their interactions in the three-dimensional space (surface) which the interaction of variables are precisely studied on response surface, especially (Montgomery. 2008). Box-Behnken design (BBD) and central composite design (CCD) are main branches in the RSM. In this work, the CCD was applied to investigate the effects of variables in adsorption of magnesium ions. Reason of this choice was low error of the CCD in analyzing of data than the BBD. Furthermore, trying to find optimum factors and responses were accomplished through the CCD. The selected variables for this research were the initial magnesium ions concentration, pH, contact time and biosorbent dosage. The variables were the most significant factors with respect to experimental conditions considered in the literature for many adsorption processes (Kyzas et al. 2019; Ogata et al. 2018). Biosorbent capacity (q) and Adsorption efficiency (R, %) were selected as the responses of experiments. The factors were coded based on three levels as the low (-1), medium (0) and high (+1). Their rang, coded levels and experimental runs are listed in Table 2 a and b. In addition, experimental and predicted results are tabulated in Table 3. Al of the experiments were carried out in triple and final value was their average. Table 2 presents twenty-one runs and five center points which were randomly specified as the experimental design based on the CCD method.

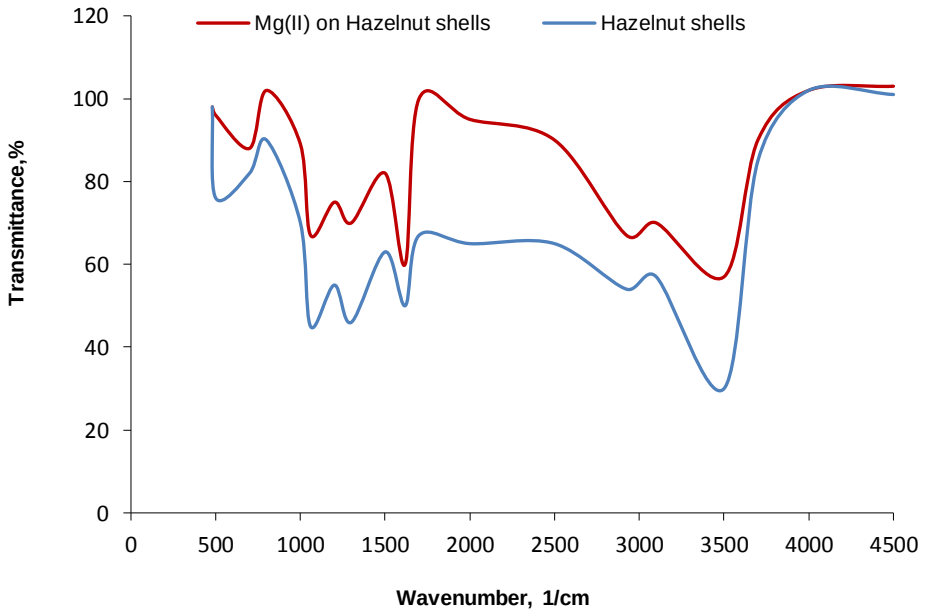


Fig. 2. FT-IR spectra before and after Mg^{2+} adsorption.

Please cite this article as: A. Raziani, A. Mohammadidoust, Modeling and optimization study by response surface methodology on magnesium ions removal from hard water through a biosorbent, Journal of Applied Research in Water and Wastewater, 7 (1), 2020, 77-89.

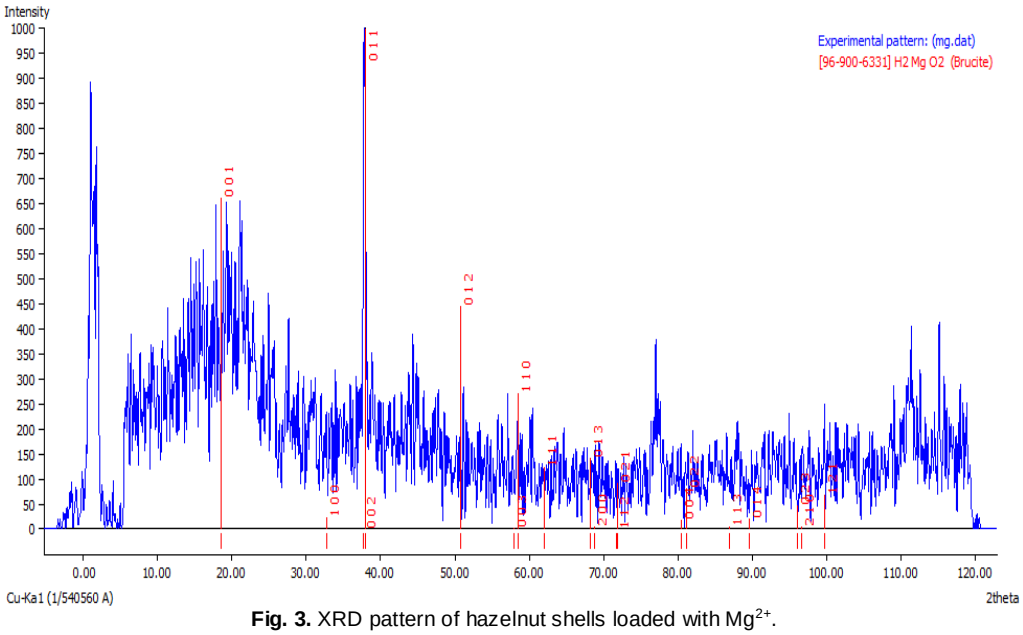


Fig. 3. XRD pattern of hazelnut shells loaded with Mg^{2+}.

Table 2a. The Variables with coded levels and the experiments based on the CCD.

Variables	Factor code	Levels		
		-1	0	+1
Initial concentration, mg/L	A	100	150	200
pH	B	4	7	10
Contact time, min	C	20	40	60
Biosorbent dosage, g	D	0.4	0.7	1

Table 2b. Experimental design.

Run no.	A	B	C	D
1	0	0	0	0
2	0	0	+1	0
3	+1	+1	-1	-1
4	0	+1	0	0
5	0	0	0	0
6	-1	-1	+1	-1
7	0	0	0	0
8	+1	-1	+1	+1
9	+1	0	0	0
10	0	0	0	0
11	-1	-1	-1	-1
12	0	-1	0	0
13	-1	+1	+1	+1
14	0	0	0	0
15	0	0	0	-1
16	0	0	0	+1
17	0	0	-1	0
18	-1	0	0	0
19	-1	+1	-1	+1
20	+1	+1	+1	-1
21	+1	-1	-1	+1

3.2.2. Response surface modeling and analysis of variance (ANOVA)

To prevent the repeated experiments and reducing the cost and time parameters, it is important to develop a good model for prediction of the responses. The RSM suggested a quadratic model due to the variables of the experiments. Because of the excess calculations and errors in estimating the outputs, the models were modified by removing non-significant parameters which explained in subsequent section. Finally, polynomial regression equations were presented as the best model in terms of coded factors as follows:

$$q=3.42+0.56A+0.61B+0.35C-0.49D+0.54AB+0.29AD-0.16CD+0.15A^2+0.47D^2 \quad (3)$$

$$R=32.07-6.5A+5.67B+2.92C+11D+3.31AB-0.69AC+2.36AD+1.69BD+2.79A^2+1.62D^2 \quad (4)$$

As reported in Table 3, predicted outputs (q, R) with respect to suggested models, have great correlation with the experimental data. These models cover the main effects, their interactions and quadratic effects on Mg^{+2} adsorption process according to capacity and efficiency. Interactions between the variables have crucial influences on the adsorption process which are investigated two variables, simultaneously.

Table 3. Experimental and predicted results for Mg^{+2} adsorption, CCD.

Run	Amount of adsorption (q), mg/g		Adsorption efficiency (R), %	
	Experimental	Predicted	Experimental	Predicted
1	3.285	3.42	30.66	32.07
2	3.78	3.77	35.33	34.99
3	5.375	5.44	21.5	21.68
4	4.07	4.03	38	37.74
5	3.428	3.42	32	32.07
6	4.625	4.7	37	37.28
7	3.428	3.42	32	32.07
8	3.45	3.44	34.5	34.9
9	4.14	4.13	29	28.36
10	3.5	3.42	32.66	32.07
11	3.75	3.68	30	30.06
12	2.857	2.81	26.66	26.4
13	2.95	2.96	59	59.28
14	3.357	3.42	31.33	32.07
15	4.375	4.38	23.33	22.69
16	3.4	3.4	45.33	44.69
17	3.071	3.07	28.66	29.15
18	3	3.01	42	41.36
19	2.6	2.58	52	52.06
20	6.5	6.46	26	26.14
21	3.05	3.06	30.5	30.44

In the past, univariate way was a conventional method in analyzing of variables, but now, mathematical and statistical methods by aiding analysis of variance play a prominent role in the detailed study of interactions. Concerning to Table 4, it was obviously understood that statistical indices are in appropriate states. For instance, the determination coefficient (R^2) of 0.9971 for the capacity (q) and 0.9968 for the efficiency implied that the models processed the responses in a level of high accuracy so that only 0.29 % and 0.32 % of total variations for q and R could not be interpreted by these models, respectively. Therefore, they will be trusted in order to forecast the Mg^{+2} adsorption from hard water as general models. Moreover, analysis of variance (ANOVA) was applied to test of the models. Degree of significance for main, quadratic and interaction effects were determined according to probability value (p-value). The variables with p-value less than 0.01 are

Please cite this article as: A. Raziani, A. Mohammadidoust, Modeling and optimization study by response surface methodology on magnesium ions removal from hard water through a biosorbent, Journal of Applied Research in Water and Wastewater, 7 (1), 2020, 77-89.

highly significant, between 0.01 and 0.05, significant and higher than 0.05 are reported as non-significant effect in statistical approaches (Mohammadidoust et al. 2016a; Montgomery., 2008). Tables 5 and 6 indicate that the models were significant for the capacity and efficiency of the adsorption process. In other words, these models are exact and credible at 95% confidence level due to data processing and rational variations regarding the variables which used in this study. Furthermore, lack of fit index had non-significant degree (greater than 0.05) for both models. It verified the validity of the models. As illustrated in the Tables 5 and 6, the main variables (linear) are in a highly significant degree for q and R responses. In the adsorbent capacity model, the interaction effect between initial concentration of magnesium ions and pH (AB), also contact time and biosorbent dosage (CD), have the highest significance among the other interactions. In addition, the second-order variable of the biosorbent dosage (D^2), noticed as the most important effect on Mg^{+2} adsorption than other second-order effects. The p-value of other variables such as AC, BC, BD, B^2 and C^2 reported as 0.1838, 0.3553, 0.8137, 0.4833 and 0.9139. Therefore, these variables were not recognized as significant effects and removed from the related model. In the adsorption efficiency model, the interactions between initial concentration with pH (AB) and biosorbent dosage (AD) show highly significant degree while AC and BD interactions are found as significant effect on the efficiency of the adsorption. In this model, second-order variable of the initial concentration of Mg^{+2} (A^2) had the most significant effect on the efficiency. The variables of BC, CD, B^2 and C^2 with p-values of 0.8458, 0.8359, 0.8012 and 0.4136 were non-significant in the adsorption efficiency. Finally, the summarized models have
been expressed in the Eqs. 3 and 4.

Table 4. Statistical indices of the predicted q and R, %.

Statistic parameters	q	R, %
Standard deviation	0.067	0.73
R-Squared	0.9971	0.9968
Adj R-Squared	0.9946	0.9935
Pred R-Squared	0.9864	0.9700
Adeq Precision	83.548	70.657
Mean	3.71	34.16
C.V.%[1]	1.80	2.15
PRESS[2]	0.23	50.05

[1] Coefficient of variation
[2] Prediction residual sum of square

3.2.3. The effects of the variables on the adsorption of Mg^{+2}

- Univariate effect

In this study, the operating parameters of the initial concentration of magnesium ions (A), pH (B), contact time (C) and biosorbent dosage (D) were investigated on the adsorption of magnesium ions at constant temperature of 25 °C. The effect of one-variable is evaluated at constant amount of other variables (medium level). As shown in Fig. 4 a and b, with increasing the initial concentration, the adsorbent capacity (q) increased while the adsorption efficiency (R, %) decreased. It is evident that by increasing the initial concentration, cations were attracted on the surface of biosorbent with negative charge. Nonetheless, negative effect on the R can be attributed the saturation of active sites of biosorbent on above places and declining the diffusion of the metal ions into the pores (Banat et al. 2000). In addition, a similar result was observed in study of Ferreira et al. (2011).

It can be significant that the pH parameter effects on ionization degree and leads to the variation of the reaction kinetic and equilibrium specifications of the processes (Aksu and Akpinar. 2001; Kumar et al. 2009). The pH is one of the important variables affecting on the adsorption processes. Its effect was determined according to the type of the adsorbent and functional groups onto the sorbent. Figs. 4 a and b reveal that increasing pH has a positive effect on the q and R responses. It may be related to competition between hydrogen and magnesium ions in ranges of the pH. Meanwhile, at higher pH, the magnesium ions overcome the hydrogen ions and adsorbed on the surface of hazelnut shells. Whereas, in acidic solution, it is clear that H^+ acts as powerful ion and well adsorbed on the biosorbent (Bingol et al. 2012). The influence of the contact time in interval of 20-60 min was studied. Enhancement of time resulted in increase the q and R which is confirmed in Fig. 4 a and b. In fact, more time provides an opportunity to contact between the adsorbent and adsorbate. In this work, maximum adsorption occurred in time of 60 min and did not any change after this time. Therefore, equilibrium time was determined in duration of 1 h. Finally, the biosorbent dosage had different effects on the capacity and efficiency of the adsorption process. It can be found in Fig. 4 a and b) that the biosorbent addition declined the adsorbed amount of Mg^{+2} in the unit mass of biosorbent. It can be interpreted by reduced concentration gradient between magnesium concentration in the solution and biosorbent surface (Bingol et al. 2012; Sud et al. 2008). Moreover, the efficiency increased by increasing the hazelnut shells (Fig. 4b). In other words, more amount of metal ions placed on the biosorbent surface and removed from the solution at constant content of magnesium ions.

- Interaction effect

To further investigate, the interaction of variables affecting on the adsorption process was studied. The interactions of two variables were considered at constant amount of two other variables (medium level). Fig. 5a depicts the interaction between initial concentration of the solution and pH. The simultaneous effect of the variables on the R is observed in the Fig. Medium contents of contact time and biosorbent dosage were 40 min and 0.7 g with taken into account the experimental design. As discussed in previous section, the negative effect of adding the initial concentration is clear on the efficiency of the process. In this figure, increasing pH repaired the negative effect of initial concentration and promoted the R, so that pH acted as a dominant effect. It should be noted that red curve indicates the high level of pH. Interaction between the initial concentration and biosorbent dosage on the R is shown in Fig. 5b. Medium levels of pH and contact time considered as 7 and 40 min, respectively. Enhancement of biosorbent increased the efficiency of the adsorption which was also mentioned earlier. As an important result, it can be understood that increasing amount of biosorbent not only increased the R but reduced the negative effect of the initial concentration on the uptake of Mg^{+2}.

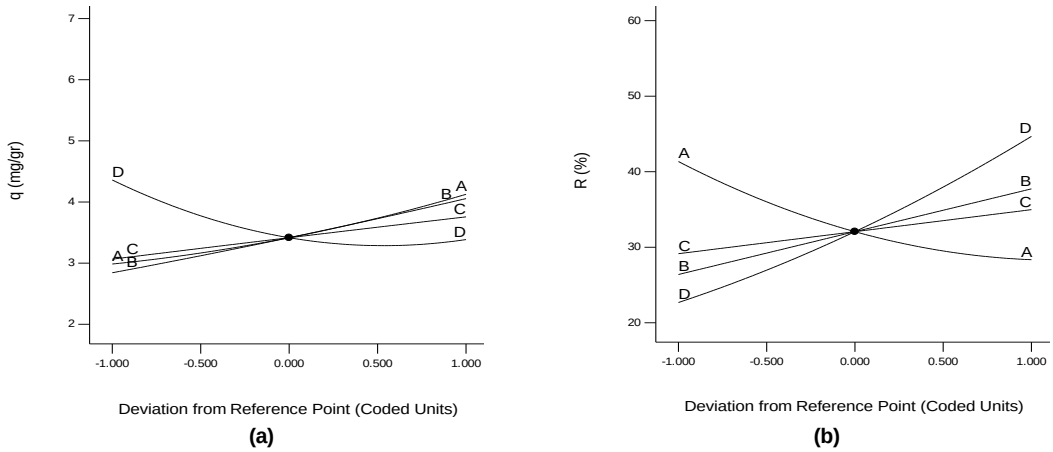


Fig. 4. The effect of each variable on the Mg^{+2} adsorption, a: biosorbent capacity (q), b: adsorption efficiency (R, %).

Please cite this article as: A. Raziani, A. Mohammadidoust, Modeling and optimization study by response surface methodology on magnesium ions removal from hard water through a biosorbent, Journal of Applied Research in Water and Wastewater, 7 (1), 2020, 77-89.

Table 5. Analysis of variance and importance of variables in the quadratic regression model of the q response.

Source	Sum of squares	df[1]	Mean square	F value	p-value, Prob > F	Degree of importance
Model	16.66	9	1.85	413.12	< 0.0001	High significant
A-C_o	3.12	1	3.12	697.18	< 0.0001	High significant
B-pH	0.74	1	0.74	164.14	< 0.0001	High significant
C-Time	1.20	1	1.20	266.95	< 0.0001	High significant
D-dosage	0.48	1	0.48	106.05	< 0.0001	High significant
AB	0.46	1	0.46	103.13	< 0.0001	High significant
AC	-	-	-	-	-	Non-significant
AD	0.13	1	0.13	29.56	0.0002	High significant
BC	-	-	-	-	-	Non-significant
BD	-	-	-	-	-	Non-significant
CD	0.20	1	0.20	43.58	< 0.0001	High significant
A^2	0.073	1	0.073	16.30	0.0020	High significant
B^2	-	-	-	-	-	Non-significant
C^2	-	-	-	-	-	Non-significant
D^2	0.71	1	0.71	157.96	< 0.0001	High significant
Residual	0.049	11	4.482E-003			
Lack of Fit	0.023	7	3.237E-003	0.49	0.8097	Non- significant
Pure Error	0.027	4	6.660E-003			
Cor Total	16.71	20				

[1]Degree of freedom

Table 6. Analysis of variance and importance of variables in the quadratic regression model of the R response.

Source	Sum of squares	df	Mean square	F value	p-value Prob > F	Degree of importance
Model	1660.24	10	166.02	307.36	< 0.0001	High significant
A-C_o	84.50	1	84.50	156.43	< 0.0001	High significant
B-pH	64.30	1	64.30	119.03	< 0.0001	High significant
C-Time	85.09	1	85.09	157.52	< 0.0001	High significant
D-dosage	242.00	1	242.00	448.01	< 0.0001	High significant
AB	17.56	1	17.56	32.50	0.0002	High significant
AC	3.78	1	3.78	7.00	0.0245	Significant
AD	8.89	1	8.89	16.46	0.0023	High significant
BC	-	-	-	-	-	Non- significant
BD	4.56	1	4.56	8.43	0.0157	Significant
CD	-	-	-	-	-	Non- significant
A^2	25.18	1	25.18	46.61	< 0.0001	High significant
B^2	-	-	-	-	-	Non- significant
C^2	-	-	-	-	-	Non- significant
D^2	8.48	1	8.48	15.71	0.0027	High significant
Residual	5.40	10	0.54			
Lack of fit	3.09	6	0.51	0.89	0.5737	Non- significant
Pure error	2.32	4	0.58			
Cor Total	1665.64	20				

Fig. 5c illustrates the interaction between the biosorbent dosage and pH at medium levels of initial concentration (150 mg/L) and contact time (40 min). The effect of each variable has been previously explained. Both the pH and biosorbent dosage had positive effect on the adsorption efficiency. Although increasing pH increased the R at all of levels of biosorbent, it was found that their interaction was less effective on the response R. Moreover, the interaction of variables on the capacity of biosorbent was also investigated. Fig. 5d shows interaction effect of initial concentration and pH on the response q. In this Fig., it is obviously observed that initial concentration works poorly along with the pH parameter, so that the intensity of uptake is evident by increasing the pH. In addition, simultaneous effect of the initial concentration and the biosorbent dosage on the q is shown in Fig. 5e. It can be seen that biosorbent dosage has a significant effect on the q. Adding the biosorbent reduced the amount of uptake in unit mass of biosorbent as mentioned earlier but its negative effect was compensated at high level of initial concentration of Mg^{+2}. Finally, interaction between contact time and biosorbent dosage was evaluated. The contact time played an important role in improving the biosorbent capacity which was previously introduced. In Fig. 5f, increasing the amount of biosorbent always has a reducing effect on the q in all of states. Concerning to the figure, the adsorbed magnesium reduced by increasing the adsorbent as the increase of time had a low effect against the biosorbent. It should be noted, to summary, important interactions were presented and other interactions were either non-significant or similar effect on the responses.

3.2.4. Numerical optimization of the adsorption process

In general, Process optimization refers to improve the performance of a system or production of a product in order to derive the most benefit. Design expert presents two methods including graphical and numerical approaches. The numerical optimization is one of the methods that used as a powerful tool in finding of optimum parameters with high accuracy and clear by aiding desirability index. In this approach, a range was considered for each variable and response. The optimization process was carried out by using the objective function. Desirability function is one of

Please cite this article as: A. Raziani, A. Mohammadidoust, Modeling and optimization study by response surface methodology on magnesium ions removal from hard water through a biosorbent, Journal of Applied Research in Water and Wastewater, 7 (1), 2020, 77-89.

the most widely used techniques in multi-response optimization which was developed by Harrington (1965). Total desirability was introduced due to geometric mean of desirability of each response according to Appendix A. The desirability value is between zero and one, indicating that optimum point is close to one (ideal value). The range of the variables is listed in Table 7. The aims of the optimization were to maximize the q and R. Design expert software reported some of experiments in the optimum condition. In Table 8, the most desirable point under the specified conditions is the first experiment due to the removal efficiency of 56.21 %, the capacity of 5.729 mg/g and total desirability of 0.862. To test the optimum conditions, five additional experiments were performed which had not selected in the design of experiments. These experiments are randomly tabulated in Table 9. As resulted in Table 10, mean error of 2.44 % and 1.68 % for the q and R, respectively, verify the high estimation power of the RSM.

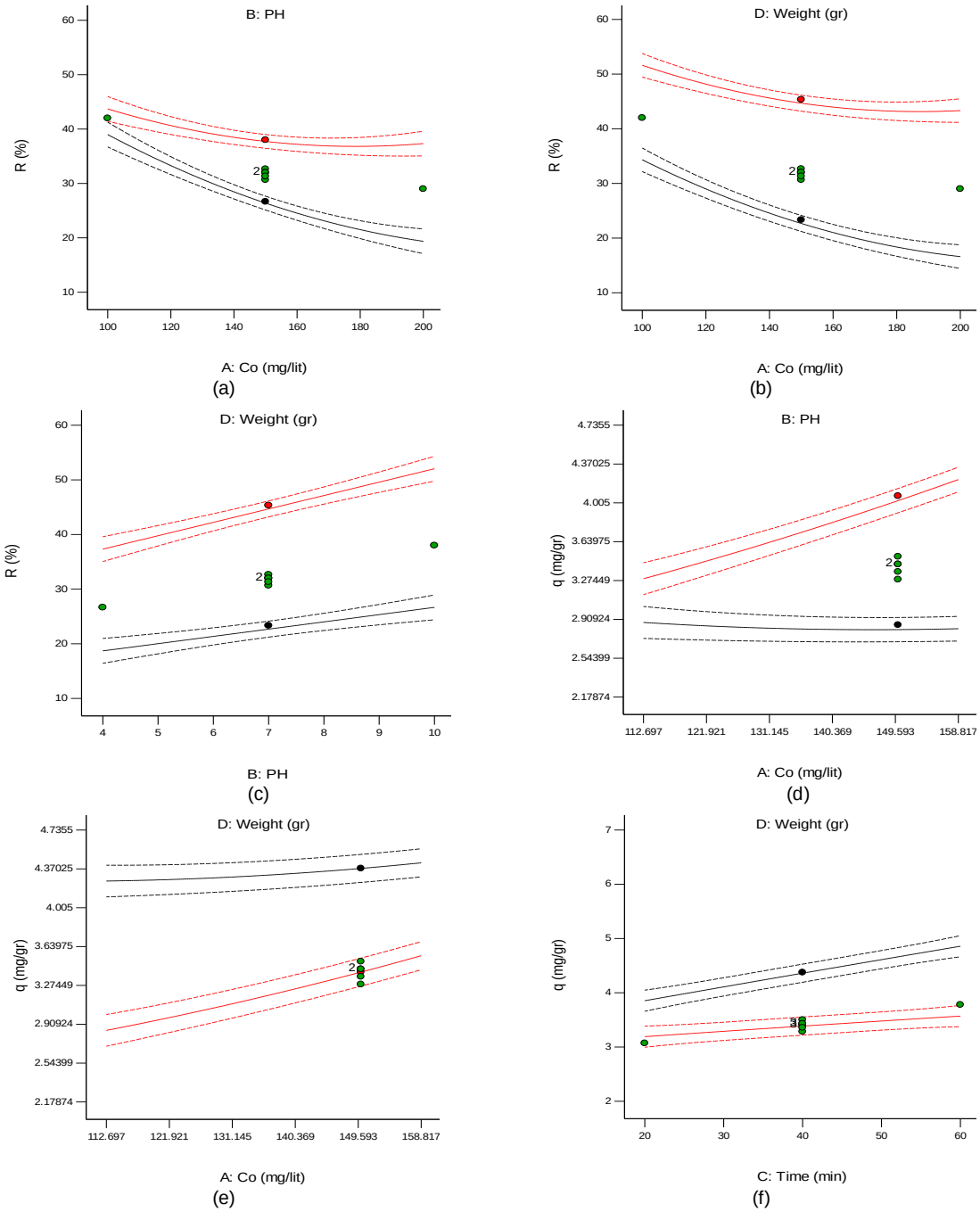


Fig. 5. Interactions between variables, a: pH and C_o on the R, b: weight of biosorbent and C_o on the R, c: weight of biosorbent and pH on the R, d: pH and C_o on the q, e: weight of biosorbent and C_o on the q, f: weight of biosorbent and time on q.

3.3. ANN modeling and comparison with the RSM

A precise prediction of the testing process can have a constructive role in reducing time and cost. The powerful tool of the artificial intelligence estimates the complex processes which have not been introduced by specified mathematical models. Artificial neural networks (ANNs) as one of the subsets of artificial intelligence were employed in this work. The MATLAB software (R2014a) used to model capacity and efficiency of the adsorption process. Initial concentration of Mg^{+2}, pH, contact time and biosorbent dosage were selected as inputs of network training. The q and R considered as outputs. The ranges of data used in the network training according to the Tables 2 and 3. The ANN choices the number of inputs and outputs as neurons of the input and output layers, respectively, while trial-and-error method determines number of neurons in hidden layer. Several algorithms consist of; Levenberg-Marquart (LM), Bayesian-Regulation (BR), Scaled conjugate Gradient (SCG) and etc., have been introduced in the ANN. Fig. 6 demonstrates the optimum algorithm and the neurons of the hidden layer. As shown in

Please cite this article as: A. Raziani, A. Mohammadidoust, Modeling and optimization study by response surface methodology on magnesium ions removal from hard water through a biosorbent, Journal of Applied Research in Water and Wastewater, 7 (1), 2020, 77-89.

the Fig., it can be found that the BR algorithm develops the network in high accuracy level against the LM and SCG algorithms. Absolute average deviation (AAD) index with a minimum value close to zero, determined the BR algorithm by 6 neurons as the best. Although the response time of the LM algorithm was shorter than the BR, it had less precision in the network training. Finally, the BR algorithm, feed-forward back propagation type and optimum architecture (4-6-2) were attained by the optimization of the network. The ANN produces the proper weights and biases and uses in an equation which is presented in Appendix A. "tansig" and "purelin" used as transfer functions of the hidden and output layers, respectively.

Table 7. The range of the variables in the optimization process.

Criteria	Target	Lower limit	Upper limit
Initial Concentration(C_o), mg/L	Is in range	100	200
pH	Is in range	4	10
Time, min	Is in range	20	60
Weight, g	Is in range	0.4	1
Amount of adsorption(q), mg/g	Maximize	2.6	6.5
Adsorption efficiency(R), %	Maximize	21.5	59

The results showed that the q and R outputs were well forecasted by the ANN model. Fig. 7a and b illustrates a comparison between the ANN and RSM approaches. In Fig. 7a, it can be seen that the RSM predicts the q data better than the ANN. In addition, as depicted in the Fig. 7b, both the ANN and RSM have good agreement with the experimental data in predicting the R output.

Table 8. The optimum experiments in the adsorption process.

Number	Co	PH	Time	Weight	q	R	Desirability
1	200.000	10.000	59.816	1.000	5.729	56.210	0.862
2	199.835	9.993	60.000	1.000	5.722	56.193	0.861
3	200.000	9.994	59.588	1.000	5.724	56.165	0.861
4	200.000	10.000	58.886	1.000	5.720	56.107	0.859
5	199.183	9.997	60.000	1.000	5.702	56.154	0.857
6	200.000	10.000	60.000	0.995	5.720	55.910	0.857
7	200.000	10.000	57.971	1.000	5.711	56.005	0.857
8	200.000	9.934	59.716	1.000	5.702	55.963	0.855
9	200.000	10.000	57.348	1.000	5.705	55.933	0.855
10	200.000	10.000	56.788	1.000	5.700	55.872	0.854
11	200.000	10.000	60.000	0.990	5.711	55.597	0.852
12	199.297	10.000	60.000	0.992	5.692	55.710	0.851
13	200.000	10.000	60.000	0.986	5.705	55.405	0.848
14	198.368	10.000	58.110	1.000	5.658	55.888	0.848
15	200.000	10.000	54.247	1.000	5.676	55.590	0.847

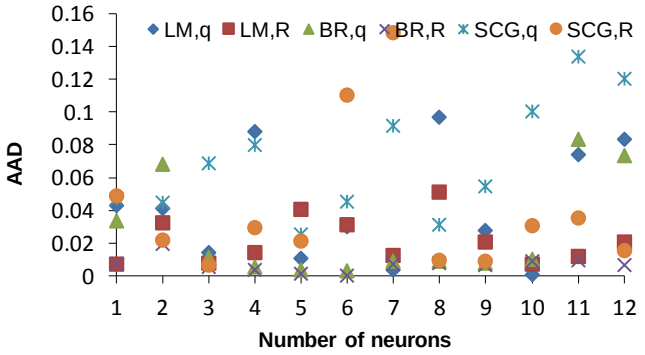


Fig. 6. The optimization of algorithm and neurons.

To more evaluation, the numerical results are reported in terms of indicators of the absolute average deviation (AAD), the average relative deviation (ARD) and total correlation coefficient (R^2). Regarding to Table 11, although both the ANN and RSM are in appropriate level of accuracy, the RSM is more exact in estimating the q. Moreover, the predicted R response is in a superior agreement with experimental through the ANN model.

Table 9. Five additional experiments to test the optimum conditions.

Number	Co	PH	Time	Weight	q	R	Desirability
1	200.000	10.000	59.816	1.000	5.729	56.210	0.862
2	200.000	10.000	60.000	0.871	5.568	48.656	0.742
3	200.000	10.000	20.006	0.901	5.108	45.912	0.647
4	150.151	10.000	58.770	1.000	4.188	54.775	0.601
5	100.005	10.000	59.975	0.400	4.824	38.600	0.510

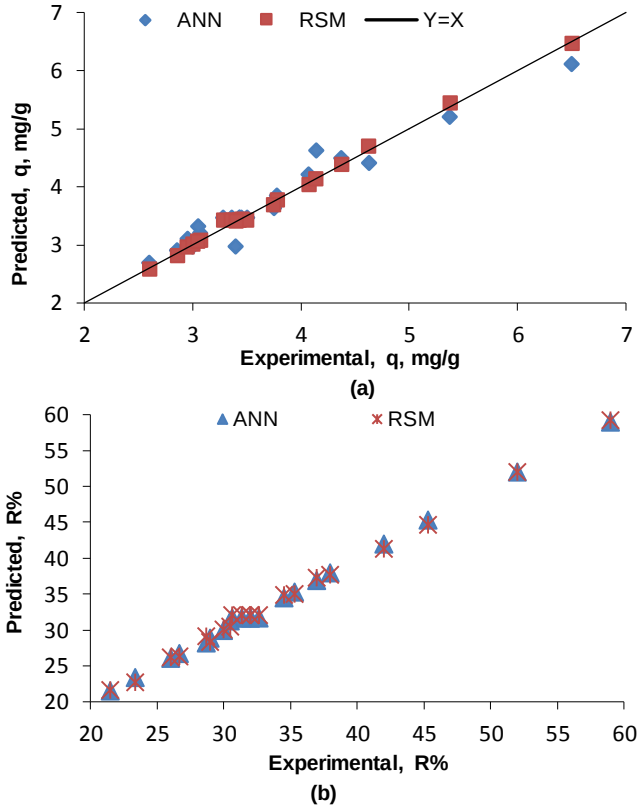


Fig. 7. The performance of the developed models, a: q, b: R %.

In summary, because of wide applications of the ANN and RSM models, they can cover the pseudo -first or second order models (e.g. kinetic models) and isotherm models (e.g. Langmuir, Freundlich) in high confidence level. For instance, the ANN acts as a comprehensive information box so that the capacity and efficiency of the adsorption process are extracted by entering the input variables.

3.4. Comparing the adsorbent capacity of the hazelnut shell with other adsorbents

In addition to the hazelnut shell, the adsorption studies of Mg ions on other adsorbents such as walnut shell have been performed and a comparison is presented in Fig. 8. The experiments were conducted at pH 7, adsorbent dosage of 0.4 g, initial concentration of 100 mg/L and time in the range of 20-60 min. As depicted in the figure, it can be understood that the hazelnut shell has a better performance than walnut shell. Although walnut shell acted as a loser biosorbent, it was found that both biosorbents can be used in removing Mg ions due to low difference of the adsorbent capacity. It should be noted that the Mg ions removal data by adsorption method were not available in the literature. Therefore, the studies were carried out by walnut shell and comparison between two biosorbent was done.

3.5. Adsorption isotherms

Determining the equilibrium state and defining a good model are principles for the adsorption process design. Adsorption isotherms can aid to investigate this state. There is a mathematical relation between the equilibrium adsorption capacity on the adsorbent surface and the equilibrium solute concentration in aqueous solution. The Mg^{+2} adsorption is dependent on the initial concentration of Mg^{+2}, significantly. To conduct the equilibrium experiments, amount of 1 g of adsorbent was added to 50 ml of the solution with pH 10 and the different initial concentration of Mg^{+2}

Please cite this article as: A. Raziani, A. Mohammadidoust, Modeling and optimization study by response surface methodology on magnesium ions removal from hard water through a biosorbent, Journal of Applied Research in Water and Wastewater, 7 (1), 2020, 77-89.

in the range of 100-200 mg/L at 25 °C. Each sample was placed on a shaker at a speed of 160 rpm. Experimental results showed that any variation of adsorption on hazelnut shell surface was not observed and time of 60 min was selected as equilibrium time. It was also presented in the experimental design as final time. Eventualy, two important equilibrium models of Langmuir and Freundlich isotherms were employed for prediction the equilibrium state. Linear form of the Langmuir isotherm is given as follows (Langmouir. 1916; Shojaeimehr et al. 2014):

$$\frac{1}{q_e} = \frac{1}{K_L q_m C_e} + \frac{1}{q_m} \quad (5)$$

where, qe (mg/g) is the equilibrium amount of Mg^{2+} adsorbed per unit mass of adsorbent, Ce (mg/L) is the equilibrium Mg^{2+} concentration in the solution, and q_m (mg/g) is the maximum Mg ions adsorption capacity. q_m indicates the maximum adsorption capacity for the adsorbent based on a monolayer coverage of metal ions that is fully covered the adsorbent homogeneous surface. K_L (L/mg) is the Langmuir constant related to the affinity of binding sites (Shojaeimehr et al. 2014).

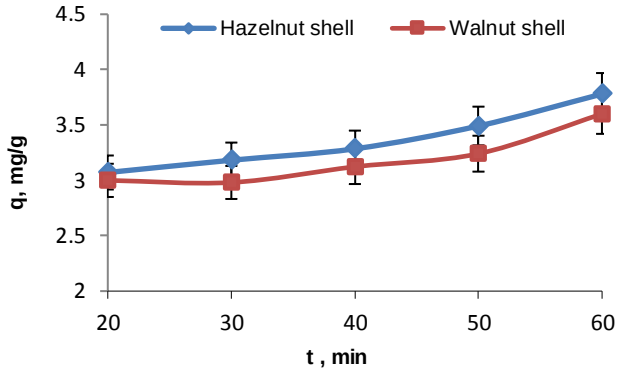


Fig. 8. A comparison between the adsorbent capacity of hazelnut shell and walnut shell (pH=7, C_0= 100 mg/L, adsorbent dosage=0.4 g).

Table 10. The accuracy of the tests.

	Amount of adsorption (q), mg/g			Adsorption efficiency (R), %		
Number	Experimental	Predicted (DOE)	Error, %	Experimental	Predicted (DOE)	Error, %
1	5.55	5.729	-3.2	55.5	56.210	-1.2
2	5.453	5.568	-2.1	47.5	48.656	-2.4
3	4.994	5.108	-2.2	45	45.912	-2
4	4.057	4.188	-3.2	54.046	54.775	-1.3
5	4.75	4.824	-1.5	38.003	38.600	-1.5
	Mean error, %		2.44			1.68

In addition. Linear form of the Freundlich isotherm is defined based on below equation (Freundlich. 1906; Shojaeimehr et al. 2014):

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \quad (6)$$

where, K_f and 1/n are the Freundlich constants that explain adsorption capacity and adsorption intensity, respectively. The Freundlich isotherm describes the heterogeneous surface (Shojaeimehr et al. 2014). Fig. 9 fits the experimental equilibrium data according to the Langmuir isotherm. As seen in the figure, the data are in good agreement with the Langmuir isotherm due to R^2 of 0.9814. In addition, q_m and K_L was calculated as 26.73 mg/g and 0.003 L/mg through slope and intercept of the plot. Fig. 10 illustrates the data fitting of the equilibrium data based on the Freundlich isotherm. It can be found that the Freundlich isotherm model develops the data in a good level with n and K_F equal 1.11 and 0.101, respectively. n value greater than unity confirms a favorable adsorption condition. Although the Langmuir isotherm is more appropriate than the Freundlich isotherm, the both models are powerful in data fitting with low error.

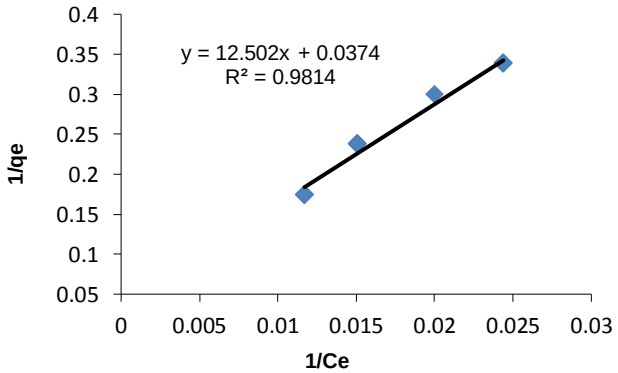


Fig. 9. The data fitting through the Langmuir isotherm model.

3.6. Adsorption kinetics

One of the important studies in the adsorption process is to investigate the influence of contact time on the amount of adsorption, which is known as kinetic studies. In this study, amount of 0.4 g of adsorbent was added to 50 mL of the solution with pH 7 and the initial concentration of Mg^{+2} 100 mg/L at 25 °C. Each sample was placed on a shaker at a speed of 160 rpm and time in the range of 20-60 min. As mentioned above, 60 min was equilibrium time.

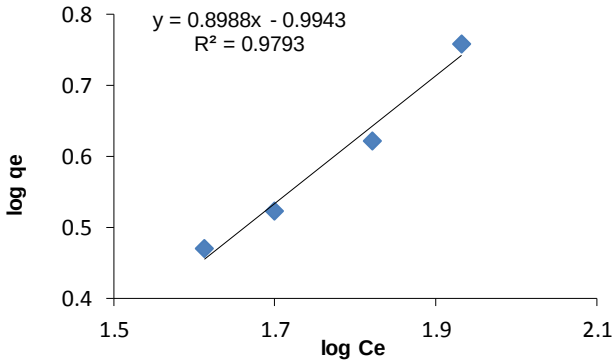


Fig. 10. The datafitting through the Freundlich isotherm model.

To interpret the adsorption kinetics, two common kinetic models including pseudo-first-order and pseudo-second-order kinetic models were employed as follows respectively (Shojaeimehr et al. 2014):

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1 t}{2.303} \quad (7)$$

$$\frac{t}{q_t} = \frac{1}{(k_2 + q_e^2)} + \frac{t}{q_e} \quad (8)$$

where, k_1 is the rate constant of pseudo-first-order adsorption process (1/min), k_2 is the pseudo-second-order rate constant of adsorption (g/mg.min). qe and q_t are the amount of metal ions adsorbed (mg/g) at equilibrium and at time t; respectively. Figs. 11 and 12 depict data fitting based on the kinetic models. Concerning to these figures, it can be found that the R^2 value of pseudo-first-order model is lower than pseudo-second-order kinetic model as the correlation coefficient of pseudo-second-order kinetic model is high and near the unity. In the pseudo-first-order model k_1 of 0.02878 and q_e of 1.36 were calculated due to slop and intercept of the plot. In addition, k_2 of -13.893 and q_e of 3.819 were determined based on the pseudo-second-order kinetic model. By comparing the two models, it can be explained that the calculated equilibrium adsorption capacity of the pseudo-second-order kinetic model ($q_{e,cal}$=3.819) was in good accordance with the experimental one ($q_{e,exp}$=3.78). Therefore, the pseudo-second-order kinetic model was capable in developing the kinetic data.

Please cite this article as: A. Raziani, A. Mohammadidoust, Modeling and optimization study by response surface methodology on magnesium ions removal from hard water through a biosorbent, Journal of Applied Research in Water and Wastewater, 7 (1), 2020, 77-89.

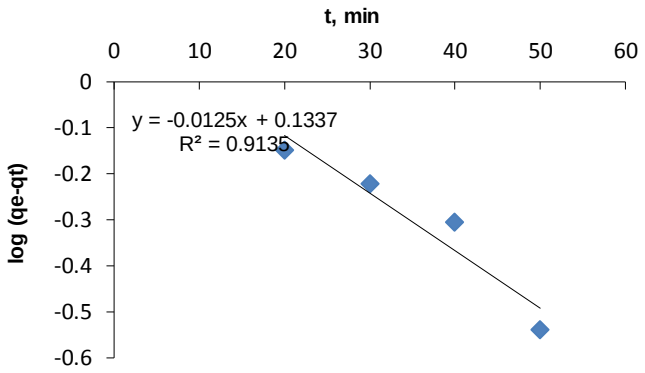


Fig. 11. The pseudo-first-order plot for Mg^{2+} adsorption capacity onto hazelnut shell.

3.7. Reusability tests of the adsorbent

The reuse of the adsorbent reduces the overall cost of the adsorption process, especially at the industrial scale. In this work, 50 ml of the magnesium solution with a concentration of 200 ppm was set at pH 10 (optimum conditions). Then, after adding 1 g of adsorbent, the solution was placed on a shaker at a speed of 160 rpm to reach equilibrium. The adsorbent was centrifugaly separated from the solution and the magnesium ions content in the solution was determined through the titration operation and the q value was calculated. The separated adsorbent was dried at 50 °C in an oven. Afterwards, the adsorbent was added to 50 ml of deionized water at pH 4.

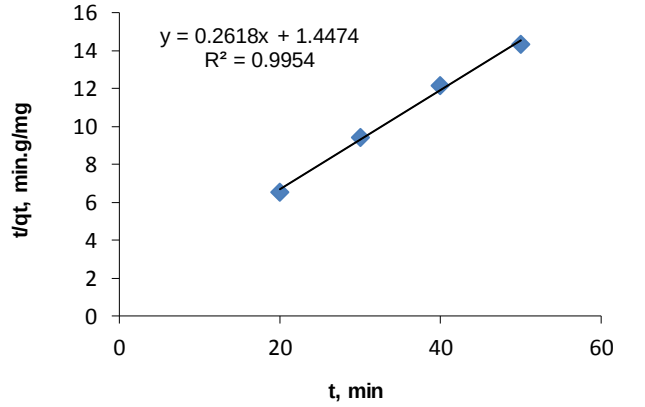


Fig. 12. The pseudo-second-order plot for Mg^{2+} adsorption capacity onto hazelnut shell.

Finally, after reaching equilibrium, the adsorbent was separated from the solution and the desorption percentage was calculated due to magnesium ions concentration. This experiment was repeated at different pH in the range of 5-10. Fig. 13 reveals the experiment results.

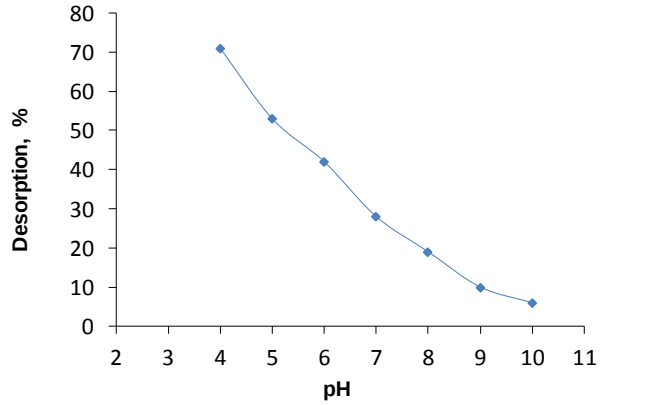


Fig. 13. The desorption percentage of the magnesium ions from the adsorbent surface at different pH.

It obviously observed that with increasing pH the magnesium ions desorption decreased. Earlier, the adsorption amount increased with increasing pH due to reasons which were mentioned. Therefore, the desorption process was confirmed in terms of variations of pH. In addition, to obtain the adsorbent potential in reusing in the experiments, some tests were implemented at the optimum conditions. The results demonstrated that the adsorbent can be reused up to 4 steps. Regarding to Fig. 14, it can be seen that the adsorbent has a good performance in reusing in the experiments as maximum performance reduction was reported by 7 %. Although the number of reusability tests was low, it was powerful in adsorbing the magnesium ions at each step.

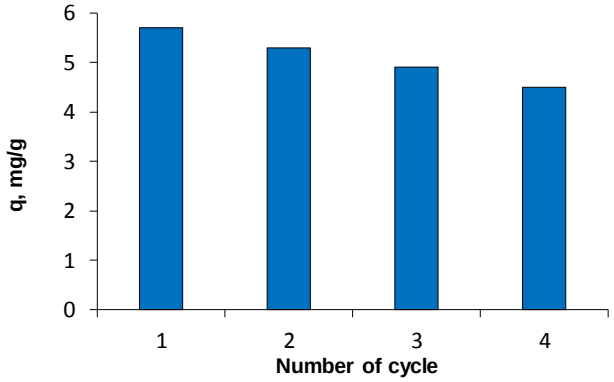


Fig. 14. Reusability tests of the hazelnut shell at optimum conditions.

4. Conclusions

This study introduced the hazelnut shell as a cheap and abundant product in nature in order to remove the magnesium ions from hard water. Reducing the Mg^{+2} led to decrease the sediments of industrial equipments. The characterizations and structure of the biosorbent were analyzed by the XRF and SEM, respectively. In addition, FT-IR and XRD analyzers confirmed the adsorption of the Mg^{+2} on the surface of the hazelnut shell as a proper biosorbent. In second part, to evaluate the effects of the variables in univariate and interaction, response surface methodology (RSM) was employed. The RSM not only developed a quadratic model but applied analysis of variance (ANOVA) for statistical investigation of the process. The performance functions (R^2=0.9971 (q), R^2=0.9968 (R %)) revealed a great model in predicting the experimental data. The numerical optimization found the removal efficiency of 56.21% and the capacity of 5.729 mg/g with a total desirability of 0.862 (initial concentration: 200 mg/l, pH= 10, biosorbent dosage: 1 g, time: 59.816 min) which was close to the experimental result. The ANN developed another model to validate and test of the RSM. Performance functions reported that the RSM and ANN excellently developed the q and R, respectively. In the present work, it can be concluded that the RSM and ANN are capable in forecasting similar adsorption processes without the use of complicated mathematical equations with a high precision. Because of the capability of hazelnut shell in Mg^{+2} reduction, it may be a competitor against other materials. Finally, the isotherm studies illustrated that the Langmuir isotherm fitted the data more appropriate than the Freundlich isotherm. In addition, the pseudo-second-order kinetic model superior described the magnesium ions adsorption kinetic.

Appendix A

a) Quadratic model

$$Y = \alpha_0 + \sum_{i=1}^{n} \alpha_i x_i + \sum_{i=1}^{n} \alpha_{ii} {x_i}^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \alpha_{ij} x_i x_j + \varepsilon \quad (9)$$

b) Total desirability

$$D = (d_1 \times d_2 \times \ldots \times d_k)^{1/k} \quad (10)$$

c) ANN model

$$Y_j = f_t\left(\sum_{i=1}^{n} w_{ji} x_i + b_j\right) \quad (11)$$

d) Performance functions

$$AAD = \frac{1}{N} \sum_{i=1}^{N} \left(\frac{y_{exp,i} - y_{model,i}}{y_{exp,i}}\right)^2 \quad (12)$$

$$ARD = \frac{1}{N} \sum_{i=1}^{N} \left(\frac{|y_{exp,i} - y_{model,i}|}{y_{exp,i}}\right) \quad (13)$$

$$R^2 = \frac{\sum_{i=1}^{N} (y_{exp,i} - y_{model,mean})^2 - \sum_{i=1}^{N} (y_{exp,i} - y_{model,i})^2}{\sum_{i=1}^{N} (y_{model,mean} - y_{exp,i})^2} \quad (14)$$

Please cite this article as: A. Raziani, A. Mohammadidoust, Modeling and optimization study by response surface methodology on magnesium ions removal from hard water through a biosorbent, Journal of Applied Research in Water and Wastewater, 7 (1), 2020, 77-89.

Acknowledgment

The authors would like to thank Islamic Azad University, Kermanshah branch, Iran, for supporting this work.

References

Aghav R.M., Kumar S., Mukherjee S.N., Artificial neural network modeling of phenol and resorcinol from water environment using some carbonaceous adsorbents, Journal of Hazardous Material 188 (2011) 67-77.

Aksu Z., and Akpinar D., Competitive biosorption of phenol and chromium (VI) from binary mixtures onto dried anaerobic activated sludge, Biochemical Engineering Journal 7 (2001) 183-193.

Al-Senani G.M., and Al-Fawzan F.F., Adsorption study of heavy metal ions from aqueous solution by nanoparticle of wild herbs, Egyptian Journal of Aquatic Research 44 (2018) 187-94.

Babel S., and Kurniawan T.A., Cr (VI) removal from synthetic wastewater using coconut shell charcoal and commercial activated carbon modified with oxidizing agents and/or chitosan, Chemosphere 54 (2004) 951-967.

Banat FA., Albashir B., Alasheh S., Hayajneh O., Adsorption of phenol by bentonite, Environmental Pollution 107 (2000) 391-398.

Bingol D, Hercan M, Elevli S., Kilic E., Comparison of the results of response surface methodology and artificial neural network for the biosorption of lead using black cumin, Bioresource Technology 112 (2012) 111-115.

Cardoso V.D.A., Souza AGD., Sartoratto P.P.C., Nunes L.M., The ionic exchange of cobalt, nickel and copper (II) in alkaline and acid-layered titanates, Colloids and Surfaces A: Physicochemical and Engineering Aspects 248 (2004) 145-149.

Castro L., Blazquez M.L., Gonzalez F., Munoz J.A., Balester A., Heavy metal adsorption using biogenic iron compounds, Hydrometalurgy 179 (2018) 44-51.

Cimino G., Passerini A., Toscano G., Removal of toxic cations and Cr (VI) from aqueous solution by hazelnut shell, Water Research 34 (2000) 2955-2962.

Desai K.M., Survase S.A., Survase PS., Saudagar P.S., LeLe S.S., Singhal R.S., Comparison of artificial neural network (ANN) and response surface methodology (RSM) in fermentation media optimization: case study of fermentative production of scleroglucan, Biochemical Engineering Journal 41(2008) 266-273.

Eccles H., Treatment of metal-contaminated wastes: why select a biological process? Trends Biotechnololgy 17(1999) 462-465.

Esalah J.O., Weber M.E., Vera J.H., Removal of lead, cadmium and zinc from aqueous solutions by precipitation with sodium Di-(n-Octyl) phosphinate, Canadian Journal of Chemical Engineering 78 (2000) 948-954.

Ferreira L.S., Rodrigues M.S., Carvalho J.C.M.D., Lodi A., Finocchio E., Perego P., et al. Adsorption of Ni^{+2}, Zn^{+2} and Pb^{+2} onto dry biomass of Arthrospira (Spirulina) platensis and Chlorella vulgaris, I. single metal systems, Chemical Engineering Journal 173 (2011) 326-333.

Freundlich H.M.F., Over the adsorption in solution, Journal of Physical Chemistry 57 (1906) 385–471.

Geyikci F., Kilic E., Coruh S., Elevli S., Modeling of lead adsorption from industrial sludge leachate on red mud by using RSM and ANN, Chemical Engineering Journal 183 (2012) 53-59.

Harington J., The desirability function, India Quality Control, 21 (1965) 494-498.

Hasan S.H., Srivastava P., Talat M., Biosorption of Pb (II) from water using biomass of aeromonas hydrophila: central composite design for optimization of process variables, Journal of Hazardous Material 168 (2009) 1155-1162.

Hong M., Yu L.Y., Wang Y., Zhang J., Chen Z., Dong L., Zan Q., Li R., Heavy metal adsorption with zeolites: the role of hierarchical pore architecture, Chemical Engineering Journal 359 (2019) 363-372.

Inspectorate D.W., Water hardness, Northern Ireland Environment Agency, 1999.

Kasiri M.B., Aleboyeh H., Aleboyeh A., Heterogeneous photo-fenton process with response surface methodology and artificial neural networks, Environmental Science and Technology 42 (2008) 7970-7975.

Khayet M., Cojocaru C., Essalhi M., Artificial neural network modeling and response surface methodology of desalination by reverse osmosis, Journal of Membrane Science 368 (2011) 202-214.

Kumar N.S., Subbaiah M.V., Reddy A.S., Krishnaiah A., Biosorption of phenolic compounds from aqueous solutions onto chitosanabrus precatorius blended beads, Journal of Chemical Technology and Biotechnology 84 (2009) 972-981.

Kyzas G.Z., Bomis G., Kosheleva R.I., Efthimiadou E.K., Favvas E.P., Kostoglou M., Mitropoulos A.C., Nanobubbles effect on heavy metal ions adsorption by activated carbon, Chemical Engineering Journal 356 (2019) 91-97.

Langmuir I., The constitution and fundamental properties of solids and liquids. Part I. solids, Journal of the American Chemical Society 38 (1916) 2221–2295.

Low K.S., Lee C.K., Leo A.C., Removal of metals from electroplating wastes using banana pith, Bioresource Technology 51(1995) 227-31.

Marshal W.E., and Johns M.M., Agricultural by-products as metal adsorbents: sorption properties and resistance to mechanical abrasion, Journal of Chemical Technology and Biotechnology 66 (1996) 192-198.

Mohammadidoust A., Rahimi M., Feyzi M., Effects of solvent addition and ultrasound waves on viscosity reduction of residue fuel oil, Chemical Engineering and Processing: Process Intensification 95 (2015) 353-361.

Mohammadidoust A., Rahimi M., Feyzi M., An optimization study by response surface methodology (RSM) on viscosity reduction of residue fuel oil exposed ultrasonic waves and solvent injection, Iranian Journal of Chemical Engineering 13 (2016a) 3-19.

Mohammadidoust A., Rahimi M., Feyzi M., Prediction and optimization of the effects of combining ultrasonic waves and solvent on the viscosity of residue fuel oil by ANN and ANFIS, Physical Chemistry Research 4 (2016b) 333-53.

Monser L., and Adhoum N., Modified activated carbon for the removal of copper, zinc, chromium and cyanide from wastewater, Separation and Purification Technology 26 (2002) 137-146.

Montgomery D.C., Design and analysis of experiments, seventh ed. John Wiley&Sons, NewYork, 2008.

Ni B.J., Huang Q.S., Wang C., Ni T.Y., Sun J., Wei W., Competitive adsorption of heavy metals in aqueous solution onto biochar derived from anaerobicaly digested sluge, Chemosphere 219 (2019) 351-357.

Ngah W.S.W., and Hanafiah M.A.K.M., Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: a review, Bioresource Technology 99 (2008) 3935-3948.

Ogata F., Ueta E., Kawasaki N., Characteristics of a novel adsorbent Fe-Mg-type hydrotalcite and its adsorption capability of As (III) and Cr (VI) from aqueous solution, Journal of Industrial and Engineering Chemistry 59 (2018) 56-63.

Pamukoglu M.Y., Kargi F., Removal of copper (II) ions from aqueous medium by biosorption onto powdered waste sluge, Process Biochemistry 41 (2006) 1047-1054.

Pavan F.A., Mazzocato A.C., Jacques R.A., Dias S.L.P., Ponkan peel: a potential biosorbent for removal of Pb (II) ions from aqueous solution, Biochemical Engineering Journal 40 (2008) 357-362.

Pedersen A.J., Characterization and electrolytic treatment of wood combustion fly ash for the removal of cadmium, Biomass & Bioenergy 25 (2003) 447-458.

Prakash N., Manikandan S.A., Govindarajan L., Vijayagopal V., Prediction of biosorption efficiency for the removal of copper (II) using artificial neural networks, Journal of Hazardous Materials 152 (2008) 1268-1275.

Please cite this article as: A. Raziani, A. Mohammadidoust, Modeling and optimization study by response surface methodology on magnesium ions removal from hard water through a biosorbent, Journal of Applied Research in Water and Wastewater, 7 (1), 2020, 77-89.

Preetha B., and Viruthagiri T., Application of response surface methodology for the biosorption of copper using rhizopus arrhizus, Journal of Hazardous Materials 143 (2007) 506-510.

Ranjan D., Mishra D., Hasan S.H., Bioadsorption of arsenic: an artificial neural networks and response surface methodology approach, Industrial and Engineering Chemistry Research 50 (2011) 9852-9863.

Rostami K., Joodaki M.R., Some studies of cadmium adsorption using aspergillus niger, penicillium austurianum, employing an airlift fermenter, Chemical Engineering Journal 89 (2002) 239-252.

Saber S., Amani-Ghadim A.R., Mirzajani V., Removal of Cr (II) from polluted solutions by electrocoagulation: modeling of experimental results using artificial neural network, Journal of Hazardous Material 171 (2009) 484-490.

Shihani N., Kumbhar B.K., Kulshreshtha M., Modeling of extrusion process using response surface methodology and artificial neural networks, Journal of Engineering Science and Technology 1 (2006) 31-40.

Shojaeimehr T., Rahimpour F., Khadivi M.A., Sadeghi M., A modeling study by response surface methodology (RSM) and artificial neural network (ANN) on Cu^{2+} adsorption optimization using light expended clay aggregate (LECA), Journal of Industrial and Engineering Chemistry 20 (2014) 870-880.

Singh K.P., Gupta S., Singh A.K., Sinha S., Experimental design and response surface methodology for optimization of Rhodamine B removal from water by magnetic nanocomposite, Chemical Engineering Journal 165 (2010) 151-160.

Sud D., Mahajan G., Kaur M.P., Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions: A review, Bioresource Technology 99 (2008) 6017-6027.

Tchobanoglous G., and Burton F.L., Wastewater engineering: Treatment and reuse, Metcalf & Eddy, Inc., 4th ed. McGraw-Hill. New York; 2003.

Turan N.G., Mesci B., Ozgonenel O., Artificial neural network (ANN) approach for modeling Zn (II) adsorption from leachate using a new biosorbent, Chemical Engineering Journal 173 (2011) 98-105.

Tyusenkov A.S., and Cherepashkin S.E., Scale inhibitor for boiler water systems, Russian Journal of Applied Chemistry 87 (2014) 1240-1245.

Wu Y., Qiu X., Cao S., Chen J., Shi X., Du Y., Deng H., Adsorption of natural composite sandwich-like nanofibrous mats for heavy metals in aquatic environment, Journal of Colloid and Interface Science 539 (2019) 533-544.

Xu D., Tan X., Chen C., Wang X., Removal of Pb (II) from aqueous solution by oxidized multiwaled carbon nanotubes, Journal of Hazardous Materials 154 (2008) 407-416.

Zhang Z., Li M., Chen W., Zhu S., Liu N., Zhu L., Immobilization of lead and cadmium from aqueous solution and contaminated sediment using nano-hydroxyapatite, Environmental Pollution 158 (2010) 514-519.

Please cite this article as: A. Raziani, A. Mohammadidoust, Modeling and optimization study by response surface methodology on magnesium ions removal from hard water through a biosorbent, Journal of Applied Research in Water and Wastewater, 7 (1), 2020, 77-89.