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Bioadsorption of Arsenic: An Artificial Neural Networks and Response Surface Methodological Approach

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Supporting Information

ABSTRACT: The estimation capacities of two optimization methodologies, response surface methodology (RSM) and artificial neural network (ANN) were evaluated for prediction of biosorptive remediation of As(III) and As(V) species in batch as well as column mode. The independent parameters (viz. pH, initial arsenic concentration, temperature, and biomass dose in the case of batch mode and bed height, flow rate, and initial arsenic concentration in the case of column mode) were fed as input to the central composite design (CCD) of RSM and the ANN techniques, and the output was the uptake capacity of the sorbent. The CCD was used to evaluate the simple and combined effects of the independent parameters and to derive a second-order regression equation for predicting optimization of the process. The sets of input−output patterns were also used to train the multilayer feed-forward networks employing the backpropagation algorithm with MATLAB. The application of the RSM and ANN techniques to the available experimental data showed that ANN outperforms RSM indicating the superiority of a properly trained ANN over RSM in capturing the nonlinear behavior of the system and the simultaneous prediction of the output.

1. INTRODUCTION

Arsenic poisoning has become a major threat to human society owing to the ever-increasing contamination of water. The presence of arsenic in the environment, its toxicity, and health hazards are well-known and have been reviewed extensively.[1−6] Because of its high toxic effects, the World Health Organization (WHO) has revised the guidelines for arsenic in drinking water from 50 to 10 μg/L.[7] However, arsenic concentrations, about 100 times more than permissible limit, are found in many parts of world including India.[1,8] Removal of arsenic from contaminated water to satisfy drinking water standards has been a challenge for water authorities. Various treatment methods are available for this purpose; however treatment cost, operational complexity of the technology, skill required to operate technology, and disposal of arsenic bearing treatment residual are factors should be considered before treatment method selection.[4,6,9,10] In this context, biosorption by inexpensive biomaterials, e.g. microbial biomass and agro-industrial residue, promises to be an excellent alternative and hence provide much more cost-effective, eco-friendly, and relatively simpler means for removal of metal ions from water.[11]

Wastewater treatments are traditionally optimized by monitoring the influence of one independent variable at a time on the experimental response while other variables are kept at a constant level. This optimization technique called "one-variable-at-a-time" analysis assumes that various treatment parameters do not interact and that the response variable is only a function of single varied parameter. However, response obtained from a waste treatment method results from interactive influences of different variables. Thus, the conventional technique does not depict complete effects of parameters on response.[12] Another disadvantage of the conventional technique are an increase in the number of experiments necessary to conduct research, leading to an increase of time and expenses as well in consumption of reagents and materials.[13] In order to overcome the limitations of the traditional method and to account for these interactive influences, multivariate statistical techniques like response surface methodology (RSM) are increasingly being used. However, RSM-based models are only accurate for predicting the relationship between the limited number of input and output parameters, which poses a limitation on its use for highly nonlinear processes,[14] such as biosorption. This has led to the use of artificial neural networks (ANN), which has come up as one of the most efficient methods for empirical modeling and optimization, especially for nonlinear multivariate systems, in the last two decades.[15,16]

Application of ANN has been considered a promising tool because of their simplicity toward simulation, prediction, and modeling. The power of ANN is that it is generic in structure and possesses the ability to learn from historical data. The main advantage of ANN compared to RSM is that ANN does not require a prior specification of suitable fitting function and it has universal approximation capability, i.e. it can approximate almost all kinds of nonlinear functions including quadratic functions, whereas RSM is useful only for quadratic approximations.[15,16] Although ANN has gained popularity for its use in various engineering fields, this approach has not been exploited for modeling and optimization of sorption process.

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In the present study, biosorptive remediation of As(III) and As(V), with the help of rice bran in both batch and continuous mode, was modeled and optimized using RSM and ANN techniques. Further, the efficiency of these models was compared.

2. THEORY

2.1. Response Surface Methodology (RSM). RSM is defined as a statistical method that uses quantitative data from appropriate experiments to determine and simultaneously solve multivariate equations.[17] Its main objective is to simultaneously optimize levels of independent variables to attain the best system performance, and thus, it is useful for developing, improving, and optimizing processes.

The most popular class of second-order designs are central composite design (CCD) which are optimized designs for fitting quadratic models[17,18] and include equal predictability in all directions from the center.[19] The total number of experimental runs (N) in CCD, with n number of variables is represented by:[20]

$$N = 2^n + 2n + n_c \quad (1)$$

where 2^n is the number of factorial runs with $2n$ axial runs and n_c center runs. Thus, for designs having four variables, N will be 31 ($n = 4$; $2^n = 16$; $2n = 8$; $n_c = 7$), and for design having three variables N will be 20 ($n = 3$; $2^n = 8$; $2n = 6$; $n_c = 6$). In full factorial CCD, all variables are studied in five levels ($-\beta$, -1, 0, $+1$, $+\beta$), actual values of which are calculated by equations given in ref 21.

For statistical calculations, variables Xi were coded as x_i as follows:

$$x_i = \frac{X_i - X_o}{\Delta X} \quad (2)$$

where x_i is the dimensionless coded value of the ith independent variable, X_o is the value of X_i at the center point, and ΔX is a step change value.

In order find a suitable approximation for true functional relationship between independent variables and a response surface, usually a second-order model is utilized in RSM because of its flexibility and ease in estimating model parameters; also there is considerable practical experience indicating that this model works well in solving real response surface problems:[22]

$$y = \beta_o + \sum \beta_i x_i + \sum \beta_{ii} x_i^2 + \sum \beta_{ij} x_i x_j + \varepsilon \quad (3)$$

where $x_1, x_2, ..., x_k$ are input factors which influence response y; β_o is constant and is the value of the response variable when the predictor variable(s) is zero. The term β_i is the linear effect of input factor x_i; β_{ii} ($i = 1, 2, ..., k$) is the quadratic effect of input factor x_i; β_{ij} ($i = 1, 2, ..., k$; $j = 1, 2, ..., k$) is the linear by linear interaction effect between input factor x_i; and ε is a residual term.

In this study, statistical and graphical software package, MINITAB Release 15 from Minitab Inc., USA, was used for regression analysis, graphical analysis, and analysis of variance (ANOVA).

2.2. Artificial Neural Networks (ANN). ANN is a computer model derived from a simplified concept of a brain. It is a parallel distribution processing system composed of nodes (neurons) and connections (weights) and is based on the principle that a highly interconnected system of simple processing elements that can learn complex interrelationships between independent and dependent variables. Neurons are single processing elements, which are connected to neurons in the next layer therefore forming different types of ANNs. The most popular ANN is Multilayer Perceptron (MLP) back-propagation ANN (BP-ANN), belonging to the class of supervised learning techniques because the method consists of comparing responses of output units to desired responses via an iterative process in which an error term is calculated and used to readjust the weights in the network in order to obtain network responses close to the desired responses. Its most important feature is the ability to learn from examples and to generalize, since the learned information is stored across the network weights. Neural networks do not require explication of a mathematical model. The final model is built through a continuous and iterative adjustment of weights which, in fact, reflect the relationship of input variables and output variables that are parameters and results in our experiments. Thus, it is not surprising that BP-ANN has gained momentum in numerous industrial and scientific areas. It is estimated that more than 90% of the neural network applications in use today employ BP-ANN or its some variants.[16,23]The adjustment of ANN parameters included the number of hidden layers and neurons, type of transfer function, learning rate, momentum, and number of patterns. A log sigmoid transfer function was used to activate neurons. The performance of ANN models was compared using root-mean-square error (RMSE) (eq 4), correlation coefficient (R^2), and T statistics (eq 5). T value measurements scattered around the line (1:1). A T value close to 1.0 indicates a good fit.[24]

$$\mathrm{RMSE} = \sqrt{\frac{1}{n}\sum_{i=1}(X_{im} - X_{ip})^2} \quad (4)$$

$$T = 1 - \frac{\sum_{i=1}^{n}(X_{im} - X_{ip})^2}{\sum_{i=1}^{n}(X_{im} - X)^2} \quad (5)$$

where n is the number of data points, X is the average of X over n samples, and X_{im} and X_{ip} are measured and predicted values of process and product parameters, respectively. The final network was selected based on the lowest error on the train and of the test data. In order to achieve fast convergence to minimal RMSE, input and output data were normalized within a range of 0.1−0.9 and as a result of all variables acquire the same weight (importance) during learning process. The normalized value (X_t) for each raw input/output data set (X_i) was calculated as[24]

$$X_t = \left[\frac{(X - X_{min})}{(X_{max} - X_{min})}\right](\mathrm{high} - \mathrm{low}) + \mathrm{low} \quad (6)$$

where X_{min} and X_{max} are minimum and maximum values of raw data, respectively, and low and high are 0.1 and 0.9 here, respectively.

In this study, Neural Network Toolbox V4.0 of MATLAB mathematical software (Matlab7, The Mathworks Inc., MA, USA) was used to predict sorption efficiency.

3. MATERIALS AND METHODS

3.1. Batch Sorption Experiments. Experiments were carried out in triplicate in Erlenmeyer flasks by adding the desired amount of rice polish in 50 mL of arsenic solutions (As(III) or As(V)) of desired initial concentration, pH, and temperature.

Table 1. CCD Matrix of Four Variables along with Experimental and Predicted Response (Uptake, μg/g) for As(III) Sorption onto Rice Polish in Batch Mode

					response (μg/g)		
run order	pH	conc (μg/L)	temp (°C)	b dose (mg)	experimental	RSM predicted	ANN predicted
1	5	800	35	1300	0.11	−0.64	0.96
2	9	400	25	1100	7.48	10.53	7.33
3	5	800	25	1300	9.27	10.24	9.27
4	5	400	25	1100	7.91	9.70	8.22
5	9	800	25	1300	13.51	16.27	13.79
6	9	800	35	1300	8.96	7.23	8.95
7	9	800	35	1100	16.50	16.25	16.70
8	9	800	25	1100	24.24	23.83	23.97
9	9	400	35	1300	7.13	10.53	7.02
10	5	400	35	1100	4.01	3.55	2.48
11	5	800	25	1100	15.76	19.88	15.56
12	9	400	25	1300	15.23	11.06	15.09
13	5	800	35	1100	6.21	10.45	6.14
14	9	400	35	1100	7.13	6.22	7.02
15	5	400	25	1300	5.61	8.16	5.37
16	5	400	35	1300	0.08	0.56	1.11
17	11	600	30	1200	1.05	3.98	1.38
18	3	600	30	1200	0.56	−4.72	0.067
19	7	1000	30	1200	21.41	18.12	21.26
20	7	200	30	1200	5.09	6.02	4.84
21	7	600	40	1200	5.04	6.83	5.29
22	7	600	20	1200	26.16	22.01	25.69
23	7	600	30	1400	6.21	8.25	6.32
24	7	600	30	1000	23.21	18.81	23.47
25	7	600	30	1200	12.61	12.78	12.69
26	7	600	30	1200	13.02	12.78	12.69
27	7	600	30	1200	12.86	12.78	12.69
28	7	600	30	1200	12.29	12.78	12.69
29	7	600	30	1200	13.00	12.78	12.69
30	7	600	30	1200	13.12	12.78	12.69
31	7	600	30	1200	12.55	12.78	12.69

The initial pH of the solution was adjusted by adding 0.1 M HCl and 0.1 M NaOH solution as required. Flasks were gently agitated in an electrically thermostatted reciprocating shaker at 200 rpm for a period of 120 min. The content of a flask was separated from the biosorbent by centrifuging at 15 000 rpm and was analyzed for remaining arsenic concentration in the sample using an Atomic Absorption Spectrophotometer (Shimadzu AA-6300). The amount of arsenic sorbed per unit mass of biosorbent (μg/g) was evaluated as

$$q_t = \frac{(C_i - C_t)XV}{W} \quad (7)$$

where, C_i and C_t are arsenic concentrations in micrograms per liter initially and at a given time t, respectively; V is the volume of arsenic solution in milliliters; and W is the weight of the biosorbent in milligrams.

3.2. Continuous Up-Flow Fixed-Bed Column Sorption Experiments. Experiments were conducted in triplicate in a borosilicate glass column with an internal diameter of 2 cm and length of 30 cm. A known quantity of biosorbent was packed in column to yield desired bed height of sorbent. This bed of sorbent was supported between two 1 cm layers of glass wool in order to prevent the sorbent from floating. Arsenic solution having the desired initial concentration was then pumped through the column at desired flow rates with the help of a peristaltic pump (Miclins PP-10) in up-flow mode at room temperature (±30 °C). Samples were collected from the outlet of the column at a time interval of 10 min until exhaustion of the column and were analyzed for their remaining arsenic concentration. Operation of the column was stopped when the effluent arsenic concentration exceeded a value of 99% of the initial arsenic concentration.

4. RESULTS AND DISCUSSION

4.1. Modeling and Optimization Using RSM. In our earlier study,[25] factors which were found influencing sorption of arsenic in batch mode were initial pH, initial arsenic concentration, biosorbent dose, and temperature. Thus, a two-level four-factor (2^4) full factorial CCD, leading to a total of 31 experimental runs, was applied for optimization of sorption in batch mode. Different levels of these variables were pH at 2, 4, 6, 8, and 10; biosorbent

Table 2. CCD Matrix of Four Variables along with Experimental and Predicted Response (Uptake, μg/g) for As(V) Sorption onto Rice Polish in Batch Mode

					response (μg/g)		
run order	pH	conc (μg/L)	temp (°C)	b dose (mg)	experimental	RSM predicted	ANN predicted
1	4	800	35	1300	10.32	11.40	10.21
2	8	400	25	1100	0.32	4.24	1.63
3	4	800	25	1300	19.32	18.86	19.16
4	4	400	25	1100	6.54	6.87	6.38
5	8	800	25	1300	3.62	7.76	4.13
6	8	800	35	1300	1.24	1.43	1.62
7	8	800	35	1100	7.54	10.86	7.51
8	8	800	25	1100	17.34	18.07	17.41
9	8	400	35	1300	0.32	3.40	1.54
10	4	400	35	1100	2.26	3.12	2.01
11	4	800	25	1100	30.35	32.27	30.12
12	8	400	25	1300	5.16	5.13	3.86
13	4	800	35	1100	23.37	23.92	23.72
14	8	400	35	1100	0.64	1.62	1.05
15	4	400	25	1300	2.98	4.66	3.68
16	4	400	35	1300	2.01	1.80	2.30
17	10	600	30	1200	0.12	−5.29	0.55
18	2	600	30	1200	7.42	7.31	7.08
19	6	1000	30	1200	26.24	23.26	26.16
20	6	200	30	1200	2.37	−0.17	2.07
21	6	600	40	1200	10.97	11.97	10.81
22	6	600	20	1200	22.24	18.88	22.52
23	6	600	30	1400	8.61	6.63	8.61
24	6	600	30	1000	21.81	18.27	21.72
25	6	600	30	1200	17.44	17.60	17.59
26	6	600	30	1200	18.02	17.60	17.59
27	6	600	30	1200	17.59	17.60	17.59
28	6	600	30	1200	17.24	17.60	17.59
29	6	600	30	1200	17.36	17.60	17.59
30	6	600	30	1200	18.21	17.60	17.59
31	6	600	30	1200	17.35	17.60	17.59

dose (mg/50 mL) at 1000, 1100, 1200, 1300, and 1400; initial arsenic concentration (μg/L) at 200, 400, 600, 800, and 1000; and temperature (°C) at 20, 25, 30, 35, and 40. In another study,[26] factors which were found affecting sorption of arsenic in continuous mode were bed height, flow rate, and initial metal ion concentration. Thus, to optimize parameters in continuous mode, a two-level four-factor (2^4) full factorial CCD, leading to a total of 20 experimental runs, was applied. Various levels of these variables were bed height (cm) at 5, 9.05, 15, 20.95, and 25; flow rate (mL/min) at 1.66, 3.01, 4.99, 6.98, and 8.33; and initial arsenic concentration (μg/L) at 100, 282.5, 550, 817.5, and 1000. Experiments were performed according to CCD experimental plan, and results thus obtained for each combination are given in Tables 1 and 2 for sorption of As(III) and As(V), respectively, in batch mode and in Tables 3 and 4 for sorption of As(III) and As(V) in continuous mode, respectively. Results were also predicted with the help of CCD of Minitab software and are given in the same tables.

Regression analysis was performed to fit response function to experimental data. The significance of regression coefficients of each parameter is determined by standard error of coefficient (SE coefficient), student's *t* test, and probability *P* values. Those effects are declared to be significant which are at a 5% probability level ($P < 0.05$). In general, the larger the magnitude of *T* and smaller the value of *P*, the more significant the corresponding coefficient term.[27] Moreover, a positive sign of regression coefficient represents a synergistic effect, while a negative sign indicates an antagonistic effect of the factor on the selected response.

Response surface regression results obtained along with a constant and coefficients (estimated using coded values) are given in Table I of the Supporting Information (SI) for biosorption of both As(III) and As(V) using batch mode and in Table II (in the SI) for biosorption of both As(III) and As(V) in continuous mode. Table I showed that values of constants were 12.7786 for As(III) and 17.6014 for As(V). These constants, representing the average uptake of As(III) and As(V) onto rice polish during batch mode of sorption which did not depend on any variable and interaction of variables, were found to be significant as they have high *T* values and low *P* values. Thus, the average uptake of As(III) by rice polish was 12.7786 μg/g and that of As(V) was 17.6014 μg/g which was independent of

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Table 3. CCD Matrix of Four Variables along with Experimental and Predicted Response (Uptake, μg/g) for As(III) Sorption onto Rice Polish in Continuous Mode

				response (μg/g)		
run order	bed height (cm)	flow rate (mL/min)	conc (μg/L)	experimental	RSM predicted	ANN predicted
1	9.05	3.01	282.5	2.81	5.77	3.71
2	20.95	3.01	282.5	13.63	17.08	14.19
3	9.05	6.98	282.5	0.08	−0.16	2.39
4	20.95	6.98	282.5	3.25	4.66	3.99
5	9.05	3.01	817.5	24.61	26.13	25.71
6	20.95	3.01	817.5	41.28	44.46	41.38
7	9.05	6.98	817.5	19.37	18.86	20.91
8	20.95	6.98	817.5	30.74	30.71	32.15
9	5.00	4.99	550.0	10.51	9.70	10.33
10	25.00	4.99	550.0	32.54	29.18	33.47
11	15.00	1.66	550.0	28.42	23.22	28.88
12	15.00	8.33	550.0	5.66	6.69	4.51
13	15.00	4.99	100.0	4.53	1.44	1.62
14	15.00	4.99	1000.0	41.55	40.48	39.63
15	15.00	4.99	550.0	18.65	18.49	18.38
16	15.00	4.99	550.0	17.99	18.49	18.38
17	15.00	4.99	550.0	18.35	18.49	18.38
18	15.00	4.99	550.0	18.46	18.49	18.38
19	15.00	4.99	550.0	18.46	18.49	18.38
20	15.00	4.99	550.0	18.34	18.49	18.38

Table 4. CCD Matrix of Four Variables along with Experimental and Predicted Response (Uptake, μg/g) for As(V) Sorption onto Rice Polish in Continuous Mode

				response (μg/g)		
run order	bed height (cm)	flow rate (mL/min)	conc (μg/L)	experimental	RSM predicted	ANN predicted
1	9.05	3.01	282.5	9.67	8.65	7.63
2	20.95	3.01	282.5	20.33	22.71	20.14
3	9.05	6.98	282.5	7.74	4.30	5.75
4	20.95	6.98	282.5	10.27	10.33	10.25
5	9.05	3.01	817.5	26.37	28.37	26.12
6	20.95	3.01	817.5	45.67	51.19	49.21
7	9.05	6.98	817.5	23.23	22.92	23.02
8	20.95	6.98	817.5	34.66	37.72	35.05
9	5.00	4.99	550.0	9.22	11.87	10.57
10	25.00	4.99	550.0	41.71	36.14	41.54
11	15.00	1.66	550.0	32.84	28.55	33.16
12	15.00	8.33	550.0	12.21	13.58	11.85
13	15.00	4.99	100.0	2.21	4.40	5.14
14	15.00	4.99	1000.0	49.14	44.03	47.50
15	15.00	4.99	550.0	21.31	20.05	19.71
16	15.00	4.99	550.0	19.09	20.05	19.71
17	15.00	4.99	550.0	19.99	20.05	19.71
18	15.00	4.99	550.0	20.19	20.05	19.71
19	15.00	4.99	550.0	19.78	20.05	19.71
20	15.00	4.99	550.0	19.45	20.05	19.71

factors set in the experiment. Table I also represented that in both the cases of As(III) and As(V) the linear term of pH was significant ($P < 0.05$) with $T = 3.169$ for As(III) and $T = 15.665$ for As(V); however, the quadratic term of pH in both cases was also found to be significant ($P < 0.05$) with $T = -5.230$ for As(III) and -7.461 for As(V). T values in the case of the

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quadratic term were higher than te linear term of pH, and they also had high values of coefficients, i.e., −13.1536 for As(III) and −16.5910 for As(V). This indicated that there was a curve relationship between pH and uptake in both cases. Thus, initially uptake increased with the increase of pH, and after attaining its maxima, it decreased with an increase in pH. High values of coefficients for the quadratic term of pH showed a high level of significance indicating the importance of this variable in biosorption process. It was also observed in both cases that responses were significantly affected by the synergistic effect of the linear term of concentration ($P < 0.05$), that meant that the uptake increased with an increase in the initial arsenic concentration. The linear term of temperature was also found to be significant ($P < 0.05$) having a negative effect on uptake in both cases, that meant uptake of both species of arsenic decreased with an increase in temperature. The linear term of biosorbent dose was also found to have a significant ($P < 0.05$) and antagonistic effect on the uptake of both As(III) and As(V), which implied that uptake decreased with an increase in biomass dose. In the case of As(V), the quadratic terms of concentration ($P = 0.015$) and biomass dose ($P = 0.034$) were also significant, but these were having a lesser value of T (−2.723 for concentration and −2.316 for biomass dose) than linear effects which indicated that the linear effects were more significant. All interaction terms in both cases were found insignificant ($P > 0.05$) except the interaction term of concentration and biomass dose ($P = 0.028$) in the case of As(III) and the interaction terms of pH and concentration ($P = 0.001$), concentration and biomass dose ($P = 0.002$) in the case of As(V).

On the basis of results of regression analysis, second-order quadratic models were proposed which are given as follows:

$$\begin{aligned}\text{As(III) uptake}(y) &= 12.7786 + 4.3500x_1 \\ &+ 6.0517x_2 - 7.5933x_3 - 5.2783x_4 - 13.1536{x_1}^2 \\ &- 0.7086{x_2}^2 + 1.6414{x_3}^2 + 0.7514{x_4}^2 + 3.1250x_1x_2 \\ &+ 1.8500x_1x_3 + 2.0750x_1x_4 - 3.2800x_2x_3 \\ &- 8.0950x_2x_4 - 1.4500x_3x_4 \end{aligned} \quad (8)$$

$$\begin{aligned}\text{As(V) uptake}(y) &= 17.6014 - 6.2975x_1 \\ &+ 11.7175x_2 - 5.0392x_3 - 5.8158x_4 \\ &- 16.5910{x_1}^2 - 6.0560{x_2}^2 - 3.7560{x_3}^2 - 5.1510{x_4}^2 \\ &- 11.5675x_1x_2 + 1.1325x_1x_3 + 3.0975x_1x_4 \\ &- 4.5975x_2x_3 - 11.2025x_2x_4 + 0.8875x_3x_4 \end{aligned} \quad (9)$$

where y is metal ion uptake (response) in micrograms per gram, x_1, x_2, x_3, and x_4 are coded values of test variables: initial solution pH (x_1), initial arsenic concentration (x_2) in micrograms per liter, temperature (x_3) in degrees celcius, and biomass dose (x_4) in milligrams per 50 mL.

The goodness of fit of the model was checked by multiple correlation coefficients (R^2). In the case of As(III) and As(V), R^2 was found to be 87.57% and 94.10%, respectively, revealing the statistical significance of regression and that only 12.43% and 5.9% of total variations was not explained by model in case of As(III) and As(V), respectively, but was being explained by residues. Relatively lower values of standard deviations, i.e., 3.36205 and 2.97287, for As(III) and As(V), respectively, between measured and predicted results showed that equation adequately represented actual relationship between response and significant variables. Predicted values of response are shown in Tables 1 and 2 for As(III) and As(V), respectively, and it was found that predicted responses were very close to experimental results.

Estimated regression analysis for sorption of As(III) and As(V) using continuous mode (Table II of the SI) showed the value of constants were 18.4834 for As(III) and 20.0419 for As(V) which were found significant having high a T value and low P value. This implied that the average uptake of As(III) and As(V) on rice polish was 18.4834 and 20.0419 μg/g, respectively, in column mode. It was also found that uptake in both cases of As(III) and As(V) was significantly affected by the synergistic effect of the linear term of bed height, implying that the uptake increased with an increase in bed height. The linear term of initial arsenic concentration was also found to significantly and synergistically affect uptake in both the cases of As(III) and As(V), showing that uptake increased with an increase in initial arsenic concentration. However, uptake in both the cases of As(III) and As(V) was significantly and antagonistically affected by the linear term of flow rate, showing that uptake decreased with an increase in the flow rate of metal ion in the column. A high value of coefficients which were 19.5198 for the linear term of the initial arsenic concentration in the case of As(III), 19.8107 for the linear term of the initial arsenic concentration, and 12.1281 for the linear term of bed height in the case of As(V) indicated the importance of these variables in biosorption. Table II also showed that the effect of all quadratic terms was insignificant in both cases of As(III) and As(V), showing that there was no curve relation between any variables and uptake of metal ion. All interaction terms in both the cases of As(III) and As(V) were found to be insignificant ($P > 0.05$).

The regression models proposed are given as follows

$$\begin{aligned}\text{As(III) uptake}(y) &= 18.4834 \\ &+ 9.7314x_1 - 8.2676x_2 \\ &+ 19.5198x_3 \\ &+ 0.9476{x_1}^2 - 3.5264{x_2}^2 \\ &+ 2.4665{x_3}^2 - 4.5747x_1x_2 \\ &+ 4.9654x_1x_3 - 0.9403x_2x_3 \end{aligned} \quad (10)$$

$$\begin{aligned}\text{As(V) uptake}(y) &= 20.0419 \\ &+ 12.1281x_1 - 7.4877x_2 \\ &+ 19.8107x_3 + 3.9512{x_1}^2 \\ &+ 1.0214{x_2}^2 \\ &+ 4.1639{x_3}^2 - 5.6597x_1x_2 \\ &+ 6.1989x_1x_3 - 0.7740x_2x_3 \end{aligned} \quad (11)$$

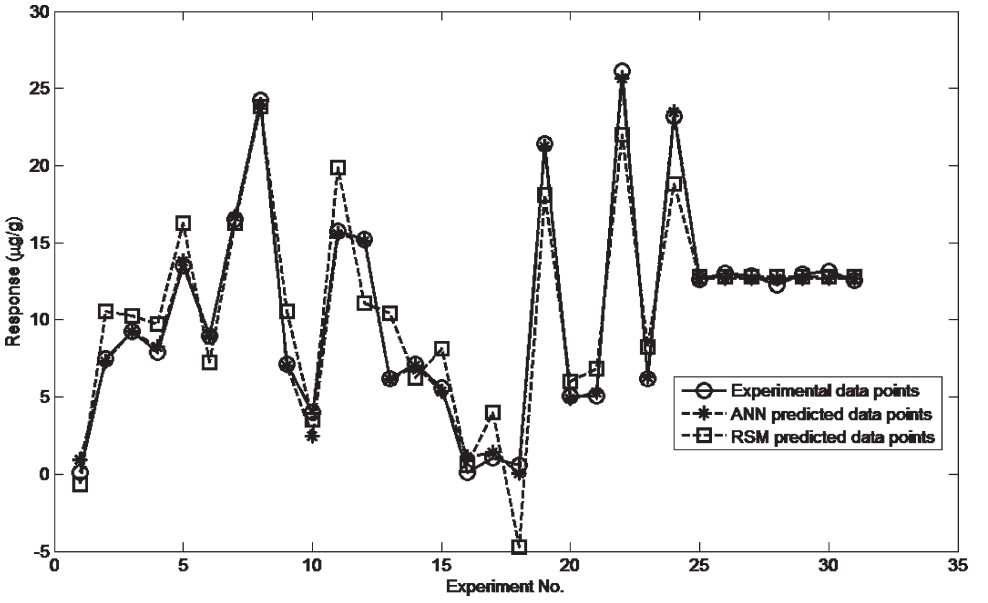
where y is metal ion uptake in micrograms per gram, x_1, x_2, and x_3 are coded values of test variables: bed height (x_1) in centimeters, flow rate (x_2) in milliliters per minute, and initial arsenic concentration (x_3) in micrograms per liter.

The values of R^2 were found to be 96.91% and 95.10% for As(III) and As(V), respectively, which revealed that the total variations which were explained by the residues are only 3.09% and 4.9% in case of As(III) and As(V), respectively. Standard deviations were found to be 2.93991 and 3.93385 for As(III) and As(V), respectively. Predicted values of responses are shown in Tables 3 and 4 for As(III) and As(V), respectively, which were found to be very close to the experimental results.

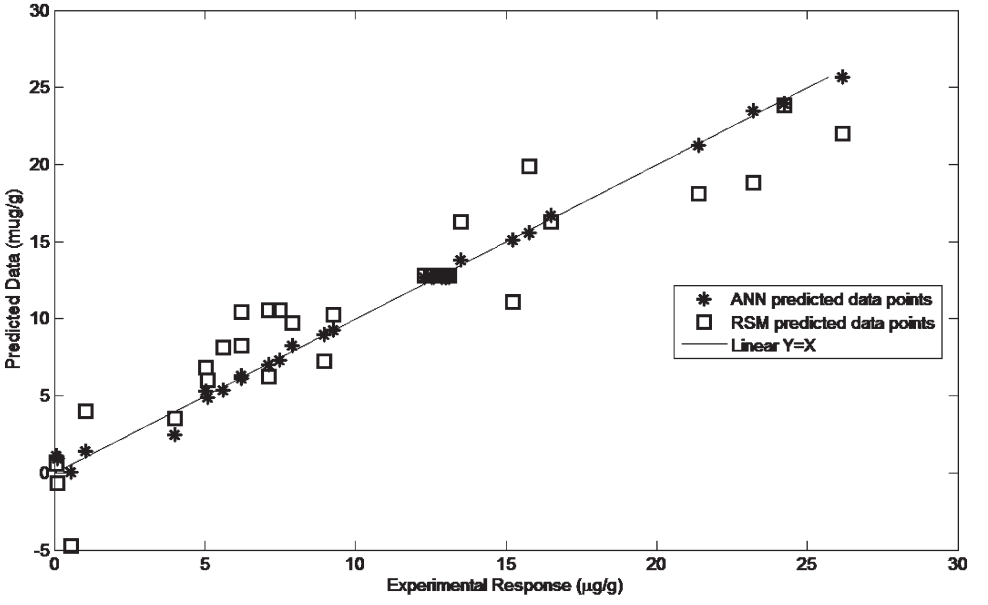
Analysis of variance (ANOVA) was performed to test the statistical significance of the F value. Table III (in the SI) showed that the F values are 8.05 and 18.21 for As(III) and

Table 5. Structure and Optimum Values of ANN Parameters Used to Predict the Biosorptive Remediation of Arsenic

LMN structure	learning rate	momentum	training MSE	maximum epochs	minimum gradient	T
4(3)−5−7−1	0.8	0.001 increment step = 10 decrement step = 0.1	2.018 × exp(−5)	15 000	1 × exp(−10)	0.95



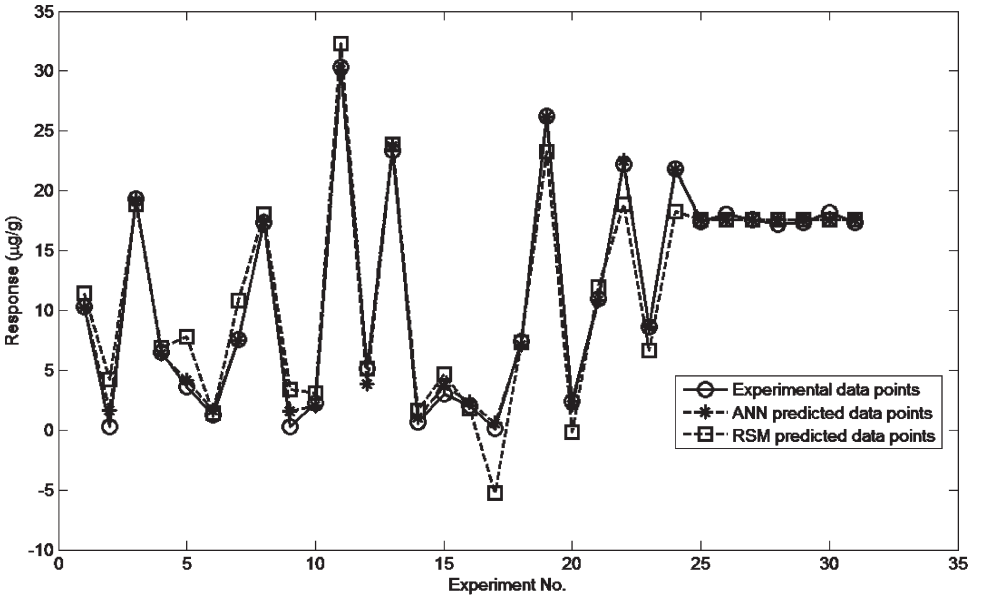
(a)



(b)

Figure 1. Comparison between the experimental and predicted data obtained by ANN and RSM models for the prediction of As(III) sorption in batch mode. (a) For each experimental run. (b) Linear plot.

As(V) sorption, respectively, in batch mode which were greater than the tabulated $F_{14,16}$ value i.e. 2.38. The F values were 34.88 and 21.55 for As(III) and As(V) sorption, respectively, in column mode (Table IV in the SI), which were greater than the tabulated $F_{9,10}$, value, i.e., 3.02. High F values indicated that the second-order polynomial models presented in eqs 8 and 9 for As(III) and As(V) sorption in batch mode and in eqs 10 and 11 for As(III) and As(V) sorption in column mode were highly



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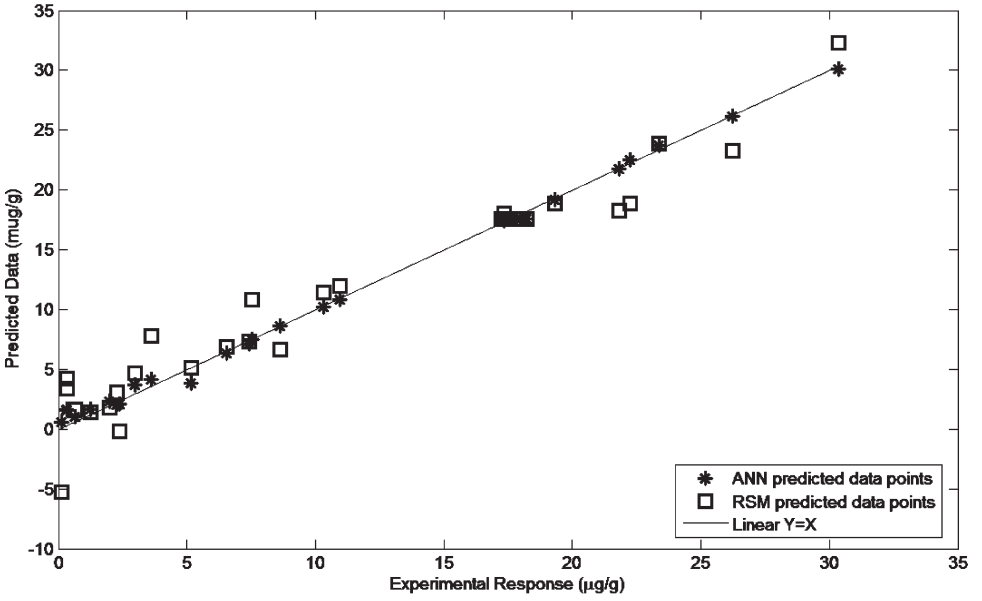
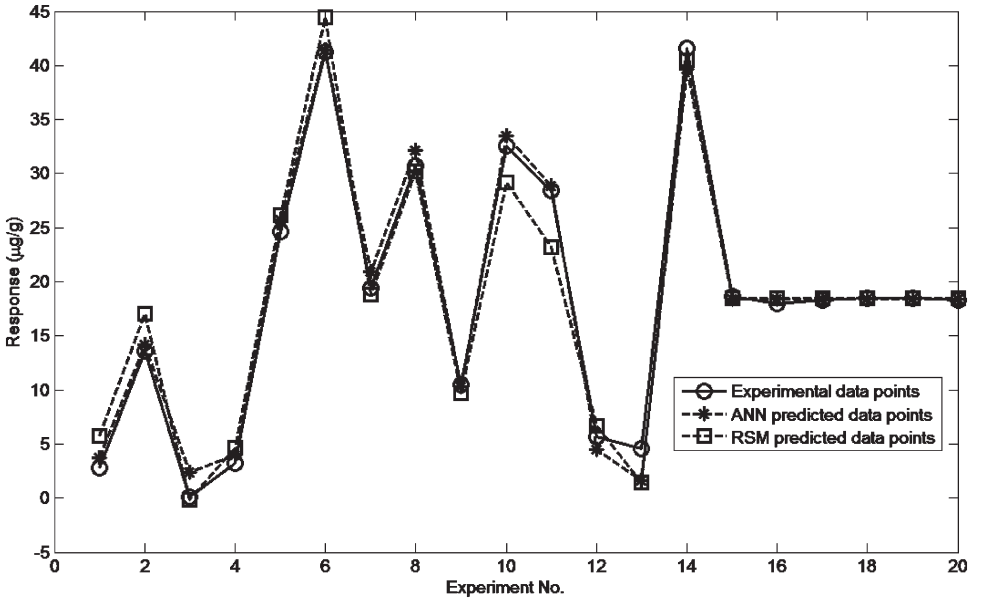


(b)

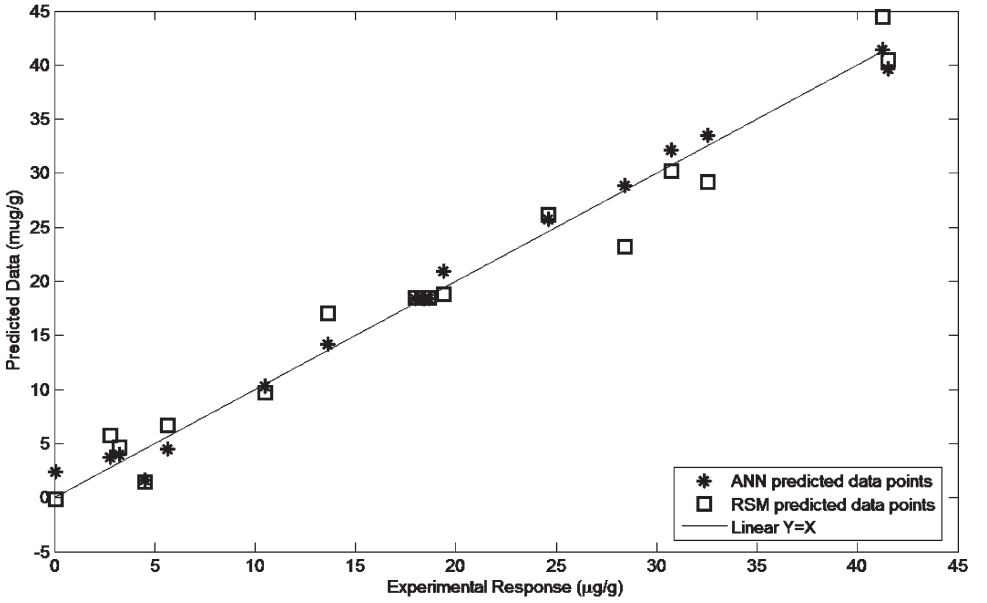
Figure 2. Comparison between the experimental and predicted data obtained by ANN and RSM models for the prediction of As(V) sorption in batch mode. (a) For each experimental run. (b) Linear plot.

significant and adequate to represent the actual relationship between response and variables. The associated Prob > *F* value for all models was lower than 0.0001 (i.e., $\alpha = 0.05$) indicating the statistical significance of models.

4.2. Modeling and Optimization Using ANN. Seeing the popularity gained by ANN in various engineering fields we have employed MLP-ANN using a Levenberg−Marquardt backpropagation learning technique for our analysis to predict experimental output. ANN have been applied for the purpose of simulation on same experimental data used for RSM. For the ANN used in this study, there were a total of 4 experiments, out of which 2 experiments were with 31 patterns, each with 5 components (*X*1, *X*2, *X*3, *X*4, *Y*1), and another 2 experiments with 20 data points each with 4 components (*X*1, *X*2, *X*3, and *Y*1), that were used for training (80% of total data points) and testing (20% of total data points) neural networks. Components represented with *X*1, etc., were input variables, whereas the other (*Y*1) was an output variable. The data were collected from experiments as explained above. The training process was run until a minimum of minimum gradient reached or minimum MSE was reached in training process. The performance of the trained network was estimated based on the accuracy of the network with test data.



(a)



(b)

Figure 3. Comparison between the experimental and predicted data obtained by ANN and RSM models for the prediction of As(III) sorption in continuous mode. (a) For each experimental run. (b) Linear plot.

The first step of ANN modeling was to optimize a neural network with the aim of obtaining an ANN mode with a minimal dimension and minimal errors in training and testing. On the basis of these criteria, the most suitable Levenberg−Marquardt backpropagation (LMN) neural network with the minimum number of neurons in hidden layers to correlate input and output parameters was selected as 4−7−5−1 (for Tables 1 and 2) and 3−5−7−1 (for Tables 3 and 4). For this structure, the best combination of ANN parameters that were used for predicting output parameters is shown in Table 5. To avoid overfitting, the maximum number of epochs was limited to 15 000. Increasing the epoch size may increase the problem of overfitting. However, LMN is a very fast learning algorithm and it is observed that the network converges to minima in less than 500 epochs.

Figures 1a, 2a, 3a, and 4a showed experimental and predicted patterns for each experimental run for As(III) sorption in batch mode, As(V) sorption in batch mode, As(III) sorption in column mode, and As(V) sorption in column mode, respectively. Testing and training samples were combined. It was observed from the figures that the neural network has approximated experimental values very efficiently; however, for some data points, the prediction is not so good.

Figures 1b, 2b, 3b, and 4b showed comparison between experimental and predicted response obtained by ANN for

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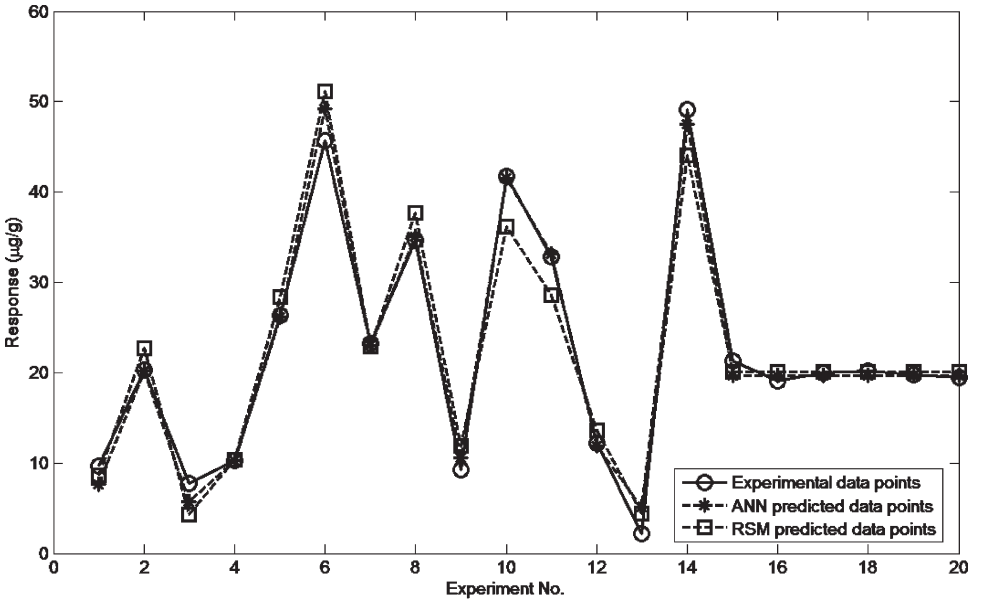
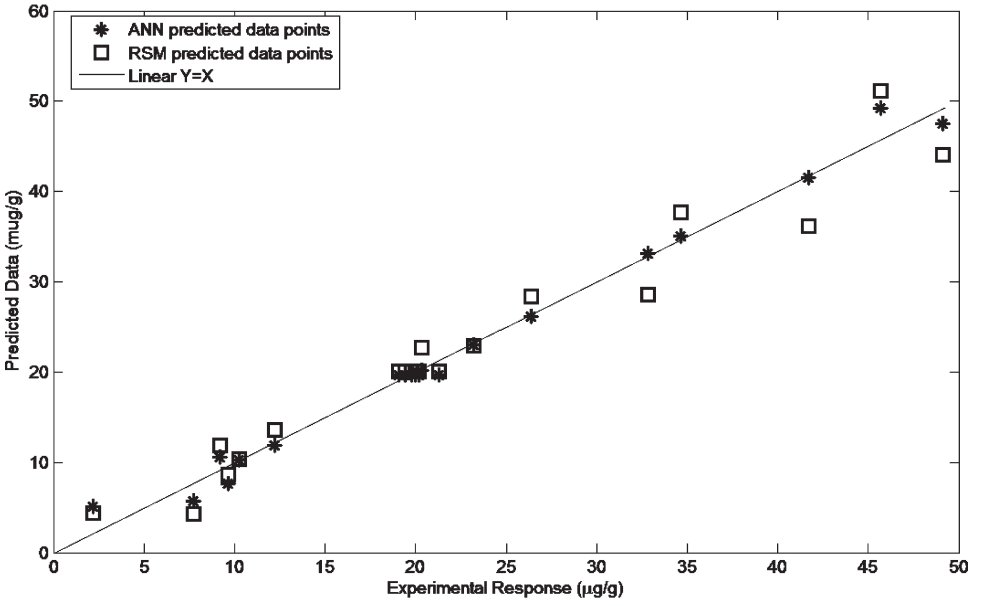


(a)



(b)

Figure 4. Comparison between the experimental and predicted data obtained by ANN and RSM models for the prediction of As(V) sorption in continuous mode. (a) For each experimental run. (b) Linear plot.

prediction with respect to a linear line for As(III) sorption in batch mode (R^2 = 0.9942), As(V) sorption in batch mode (R^2 = 0.9980), As(III) sorption in column mode (R^2 = 0.9985), and As(V) sorption in column mode (R^2 = 0.9952), respectively. The points close to the straight line showed better prediction. The very good values of R^2 between ANN predicted response and experimental response in all the cases suggest that the newly constructed ANN, which was trained using experimental data, was precise in predicting sorption of As(III) and As(V) in both batch and column mode for new experimental conditions. Another advantage of newly constructed neural network model is its accuracy to predict sorption response for any pH, biomass doses, initial arsenic concentration, and temperature in the case of batch mode and any bed height, flow rate, and initial arsenic concentration in the case of continuous mode within the ranges studied and also for new experimental conditions outside the studied range.

4.3. Comparison of RSM and ANN Models. ANN and RSM models were compared for design of experiment (DoE), using which both models were trained. Experimental and predicted values of response by ANN as well RSM model are tabulated in Table 1, 2, 3, and 4 for As(III) sorption in batch mode, As(V)

Table 6. Comparison of the Predictive Capacities of RSM and ANN

	correlation coefficient (R^2)		MAE		RMSE	
data index	ANN	RSM	ANN	RSM	ANN	RSM
Table *1*	0.9942	0.9751	0.7297	0.9711	0.1378	2.4703
Table *2*	0.9980	0.9331	0.1390	0.6910	0.1574	2.1083
Table *4*	0.9985	0.9708	0.0162	0.0527	0.0331	2.0829
Table *5*	0.9952	0.9843	0.0106	0.0053	0.0836	2.7810

sorption in batch mode, As(III) sorption in column mode, and As(V) sorption in column mode, respectively. The predicted values of uptake, with the help of RSM and ANN in case of sorption of As(III) and As(V) onto rice polish in both batch and column mode were found to be in good accordance with those obtained using experiments according to the DoE. The predicted optimum values of the variables for the maximum uptake of these metal ions in both batch and column mode were also found to be in very good agreement with those obtained in our earlier studies[25,26] where the conventional one-variable-at-a-time technique was adopted to optimize the variables for the maximum uptake of As(III) and As(V) in batch and continuous column mode. This proves the applicability of RSM and ANN in the prediction and optimization of the biosorption process with minimum amount of experimental setup and thus minimum consumption of reagents which in turn reduces the treatment cost. Though both models based on RSM and ANN preformed well and offered stable responses in predicting combined interactions of independent variables with respect to response, the ANN-based approach was better in fitting to measured response in comparison to the RSM model. The comparative parity plot for ANN and RSM predictions for DoE is represented in Figures 1b, 2b, 3b, and 4b for As(III) sorption in batch mode, As(V) sorption in batch mode, As(III) sorption in column mode, and As(V) sorption in column mode, respectively. The MLP-based model had fitted experimental data with an excellent accuracy, and RSM-based prediction shows greater deviation than ANN. The comparative values MAE, RMSE, and R^2 are given in Table 6. In our experiments, ANN has shown significant higher generalization capacity than RSM. This higher predictive accuracy of ANN can be attributed to its universal ability to approximate nonlinearity of the system whereas RSM is only restricted to a second-order polynomial. Another advantage of ANN over RSM can be stated as its ability to calculate multiple responses in a single process. To obtain a multiresponse optimization, the RSM model must be run several times (equal to the number of parameters to be predicted).

5. CONCLUSION

In this work, ANN and RSM methodologies were employed for optimization of biosorptive remediation of arsenic. The ANN model was compared to RSM model for its modeling and predictive abilities. ANN showed better accuracy and predictive ability than RSM even with a limited number of experiments. Although, RSM was found useful for directly obtaining insight into system (e.g., interactions between different components), because of its structured nature, is has consistently performed better than RSM in all aspects. It is also very important for a prediction method to perform consistently. ANN is inferior in that scenario since they require proper training. They are also not able to make any decision about available training data. Including some preprocessing techniques that can take care of this task will improve overall performance of prediction. Thus, it can be concluded that even though RSM is most widely used method for sorption optimization, the ANN methodology may present a better alternative.

■ ASSOCIATED CONTENT

Supporting Information. Table I, II, III, and IV. This information is available free of charge via the Internet at http://pubs.acs.org/.

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