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# A novel method to identify optimized parametric values for adsorption of heavy metals from waste water

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ABSTRACT

In the present study, a strategy to obtain the optimum parameters for the removal of metal ions from wastewater is developed. A generalized model is proposed which can be used to represent the dependence of the dependent parameter on the independent parameters. Here, the experimental data from various studies available in the literature are utilized for the development of the model. The experimental data are normalized on the basis of their maximum value considered among all the experiments in the study. The normalized data are further non-linearly regressed to a fourth-order polynomial using Microsoft Excel 2007 to obtain the model equation. The model equation is developed indicating the dependence of dependent parameter (adsorption capacity) on the independent parameters (initial metal concentration, pH, contact time and adsorbent dosage). The proposed generalized equation is validated using various experimental results from the literature and the parameters of the model equation are being estimated. The modeled equation is later being optimized by applying a specific optimization technique (differential evolution). A code of differential evolution is being developed using the platform of MATLAB 7 for the optimization of the models.



## 1. Introduction

There are various studies reported in the literature for the removal of heavy metals using large number of adsorbents [1–5]. Most of the studies are performed to evaluate the performance of the adsorbent for the removal of specific metal ion. The common trend followed by most of the researchers is that, the effect of a parameter is examined by varying the specific parameter keeping the others constant. However, few studies have been found where the researchers have sampled to obtain the optimal parameters on which the removal efficiency of the adsorbent is maximum, considering the dependent parameters all together [6–10]. There is a need to propose a mathematical equation which can be used by most of the studies described in the literature to produce an optimal set of parameters resulting in the maximizing of the removal efficiency or adsorption capacity.

Modeling of the equation will help the researchers to know well in advance the behavior of the adsorbent for the specific parameters. This makes a process more efficient and makes the researcher/engineer to understand the behavior of the process well in advance. This also directs to an increment in the modeling of the process which will later also serve in the process development, scaling up and optimization of the operations. In the present conditions, in this respect, is a desperate need to optimize the process, nonetheless, the objective of the optimization can vary from the minimization of the cost, energy consumption to maximizing the performance, profit or efficiency. It has as well become significantly vital because of the limitations on the time and resources. In a number of cases, even one has to gratify with the suboptimal or yet viable solutions which are safe enough and realistically attainable in a reasonable time scale.

In contrast, the modern process designing is majorly based on the computer simulations which are time consuming in nature, still after the availability of more computing power. Increasing simulation cost is too appealing to determine out a more expert and economical way out to attain an acceptable plan within a sensible time limit. This can be done by using auxiliary models which are inhabiting certain knowledge of the system under consideration and simultaneously taking care of the cost perspective of the process [11,12].

The adsorptive removal of heavy metals depends on several parameters such as initial metal concentration, adsorbent dosage, contact time and initial pH of the solution [13,14]. The result of various parameters can be assessed by performing several sets of

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batch experiments. The observational data obtained by performing experiments can be used to achieve a model which can help in forecasting the behavior of the adsorbent for the metal removal. Various methods such as non-linear regression, artificial neural network (ANN), etc. are available for the development of modeling equation with the use of experimental data. ANN is a method which is preferred for very complex systems. However, the present system is not too complex, so non-linear regression method is preferred here to develop the model equation. Also, the coefficient of determination for the non-linear regression method is good enough to use it as the model prediction method. The modeled system can be optimized to give the optimum values which can be used to give the best result in terms of removal efficiency or the adsorption capacity. There are various methods available for the optimization such as response surface methodology, factorial design, differential evolution, etc. [7,10].

Hence, the present study deals with the development of a mathematical equation which can be used to describe the relation of different independent parameters (initial metal concentration, pH, time and mass of adsorbent) with the dependent parameter (adsorption capacity). The optimization of the developed mathematical equation is carried out by using appropriate optimization technique (differential evolution (DE)).

## 2. Conceptualization of the model

In process analysis, modeling is fetching an exceptional interest. It is essential for forecasting the response and behavior of the system on the basis of reliant input parameters. We have tested the model with the second and higher order polynomial equations and found that the model is more better aligned with the experimental results when the order of the polynomial is kept at 4 or higher. In the present study, the polynomial of fourth order (Eq. (1)) is utilized to anticipate the response of the system in terms of the adsorption capacity of the adsorbent.

$$q_{\text{pre}} = a_0 + \sum a_{i1}X_i + \sum a_{i2}X_i^2 + \sum a_{i3}X_i^3 + \sum a_{i4}X_i^4 \quad (1)$$

where $i$ represents the number of independent variables and can vary from 1 to $n$ depending on the number of parameters, $q_{\text{pre}}$ represents the predicted adsorption capacity, $a_0$ represents the intercept coefficient and $a_{i1}$, $a_{i2}$, $a_{i3}$ and $a_{i4}$ are the constants for 1st, 2nd, 3rd and 4th order variables and $X_i$ represents the normalized value of $i$th dependent variable.

The experiments are to be done to get the essence of individual parameters on the adsorption capacity of the adsorbent. The observational data obtained for each parameter is taken to be normalized on the basis of maximum parameter value considered in all the experimentations. The normalized values can be regressed using Microsoft Excel 2007 to fit the fourth order polynomial. This will present a mathematical model which will be satisfied predicting the adsorption capacity of the adsorbent on substituting the various parameters.

For the present study, we have considered four independent parameters viz. the inlet concentration ($C_{\text{in}}$), pH, contact time and adsorbent dosage on which the adsorption capacity depends. The present model may also be utilized for other independent parameters such as temperature, particle size, etc. to get the optimum parametric values. However, this study is limited to four parameters which are more commonly reported in various studies.

For instance, in the maiden set of readings the inlet concentration is varied, keeping the other parameters such as pH, contact time and mass of the adsorbent constant. Likewise, more data are recorded by changing one of the parameters and by keeping other input parameters to be perpetual. The experimental values are later being regressed using Microsoft Excel and will present an equation which can be represented by Eq. (2).

$$\begin{aligned} q_{\text{pre}} = {} & a_0 + a_{11}X_1 + a_{21}X_2 + a_{31}X_3 + a_{41}X_4 + a_{12}X_1^2 + a_{22}X_2^2 \\ & + a_{32}X_3^2 + a_{42}X_4^2 + a_{13}Z_1^3 + a_{23}X_2^3 + a_{33}X_3^3 + a_{43}X_4^3 + a_{14}X_1^4 \\ & + a_{24}X_2^4 + a_{34}X_3^4 + a_{44}X_4^4 \end{aligned} \quad (2)$$

where $X_1$, $X_2$, $X_3$ and $X_4$ are the independent input parameters, the inlet concentration ($C_{\text{in}}$), pH, contact time and adsorbent dosage respectively. Also the $a_0$ is the intercept coefficient and $a_{1i}$, $a_{2i}$, $a_{3i}$ and $a_{4i}$ are the coefficients for the first order, second order, third order and fourth order variables respectively.

**Table 1**
The list of adsorbent systems considered for validation of the model.

| Adsorbent | Metal removed | References |
|---|---|---|
| Activated tamarind seeds | Cr(VI) | [15] |
| Activated fly ash | Cr(VI) | [16] |
| Activated neem leaves | Cr(VI) | [17] |
| Saw dust | Cr(VI) | [18] |
| Activated neem bark | Cr(VI) | [19] |
| Pomegranate peel | Pb(II) | [20] |
| Pomegranate peel | Cu(II) | [20] |
| Kaolinite clay | Fe(III) | [21] |

## 3. Substantiation of the model

The proposed model is not complete unless a proper validation of it is performed using reported experimental results. These types of modeling equations can be applied in several schemes where the aim is to identify a particular variable according to the variance of the independent input variables.

In the present work, the proposed modeling equation is validated using the batch adsorption experimental data obtained from the various literatures. The selection of adsorption systems which are employed here to validate the model are tabulated in Table 1.

For a sample modeling, the experimental results obtained for the Cr(VI) removal using tamarind seeds are utilized. The complete set of the experimental results is provided in Table 2 [15].

The range of parameters selected are 40–400 mg $L^{-1}$ for initial Cr(VI) concentration, 4–16 g $L^{-1}$ for adsorbent dosage, 0–58 h for contact time and 1–11 for pH value of the solution. The data for each set is normalized between 0 and 1 considering the maximum values as the base, i.e. 400 mg $L^{-1}$, 16 g $L^{-1}$, 58 h and 11 for initial concentration, adsorbent dosage, contact time and pH respectively. The normalized values are used for the regression. The regression using Microsoft Excel 2007 is performed for second order (with and without interaction), third order and fourth order polynomial. It is observed by the Annova analysis that the fourth order equation is adequately validating the experimental outcomes. The coefficient of determination ($R^2$) is found to be maximized for the fourth order in comparison to second order (with and without interaction) and third order whose values are 0.9457, 0.9378, 0.9212 and 0.9343 respectively. Also from the $F$-value of the analysis is also supporting the use of fourth order polynomial as the value of $F$ for fourth order is least as compared to second order (with and without interaction) and third order for whom the values are 44.6345, 80.4093, 71.5805 and 53.3449 respectively. Thus, for the model prediction and optimization of the process, the fourth order polynomial shown in Eq. (3) is applied.

$$\begin{aligned} q_{\text{pre}} = {} & 3.1685 + 0.4146X_1 - 1.3087X_2 + 3.2157X_3 - 25.1630X_4 \\ & + 2.2244X_1^2 + 4.1276X_2^2 - 11.0399X_3^2 + 67.8843X_4^2 \\ & - 2.8455X_1^3 - 5.7101X_2^3 + 14.6786X_3^3 - 76.5421X_4^3 \\ & + 0.9935X_1^4 + 2.6397X_2^4 - 6.5224X_3^4 + 30.4379X_4^4 \end{aligned} \quad (3)$$