

# Biochar performance evaluation for heavy metals removal from industrial wastewater based on machine learning: Application for environmental protection

Amir Dashti <sup>a</sup>, Mojtaba Raji <sup>a</sup>, Hossein Riasat Harami <sup>b</sup>, John L. Zhou <sup>c,\*</sup>, Morteza Asghari <sup>a,d,\*</sup>

<sup>a</sup> Separation Processes Research Group (SPRG), University of Science and Technology of Mazandaran, Behshahr, Iran

<sup>b</sup> Department of Chemical and Biological Engineering, The University of Alabama, Tuscaloosa, AL 35487, USA

<sup>c</sup> Centre for Green Technology, School of Civil and Environmental Engineering, University of Technology Sydney, NSW 2007, Australia

<sup>d</sup> UNESCO Chair on Coastal Geo-Hazard Analysis, Tehran, Iran

## ARTICLE INFO

### Keywords:

Biochar  
Heavy metals  
Machine learning  
Modeling  
Wastewater treatment

## ABSTRACT

Industrial wastewaters contaminated with heavy and toxic metals cause serious risks to human health and other forms of life. The performance of biochar for the elimination of heavy metals has been acclaimed. It is highly advantageous to develop efficient computational methods to predict its biosorption performance. In this research, the performance of four types of machine learning methods including adaptive neuro fuzzy inference system (ANFIS), coupled simulated annealing-least squares support vector machine (CSA-LSSVM), particle swarm optimization-ANFIS (PSO-ANFIS) and genetic programming (GP) was evaluated. The modeling was conducted on 44 types of biochar reported in 353 datasets from heavy metal adsorption experiments. All four models have demonstrated good predictive performance, especially by LSSVM, GP and PSO-ANFIS procedures. The correlation coefficient ( $R^2$ ) values of test dataset for ANFIS, CSA-LSSVM, PSO-ANFIS, and GP were 0.9428, 0.9832, 0.9712 and 0.9750. The values of mean squared error (MSE) and average absolute relative deviation (AARD) were 0.0020 and 0.36 for CSA-LSSVM model which has the superior capability than other models. The sensitivity analysis showed that the key parameters in heavy metal removal by biochar were the concentration ratio of heavy metals/biochar and total carbon content in biochar. A MATLAB code was developed to estimate the biosorption efficiency. Novel equation based genetic programming assists researchers to predict sorption yield of heavy metals by reducing the costs and time. Analyzing the results of this research can increase the understanding of researchers towards the effective remediation of hazardous chemicals in water resources.

## 1. Introduction

Thermal degradation methods can be utilized to produce biochar from the carbon-rich biomass [1]. Among dissimilar preparation methods, pyrolysis is the most common heating procedure. Different crude materials including agricultural waste, municipal solid waste, industrial by-products, and sewage sludge can be utilized for producing biochar. Biochar has been widely used in increasing soil fertility and carbon removal [2], bioenergy production [3] and environmental bioremediation [4]. Extensive research has been conducted to improve the functionality and capacity of biochar towards pollutant removal through modification and functionalization [5]. In comparison to organic pollutants which are biodegradable, the inorganic pollutants (primarily heavy metals) are not biodegradable and tend to pass through

the food chain via bioaccumulation and biomagnification. It is important to eliminate these persistent pollutants from water and wastewater streams for protecting the human and ecosystems from adverse biological effects.

In order to meet the water quality standards for heavy metal pollutants, different treatment methods such as activated carbon adsorption [6], electrocoagulation [7], ion exchange [8], and nanofiltration [9] have been utilized in water and wastewater treatment processes. Many of such methods are considered to be robust and reliable for metal removal, however, most of them are costly. Thus, it is important to develop metal removal technologies which are effective, relatively inexpensive, and sustainable, for which biochar is a good candidate [10].

Biochar has shown preferable ability to remove organic pollutants

\* Corresponding authors.

E-mail addresses: [Junliang.zhou@uts.edu.au](mailto:Junliang.zhou@uts.edu.au) (J.L. Zhou), [asgharimore@gmail.com](mailto:asgharimore@gmail.com), [asghari@mazust.ac.ir](mailto:asghari@mazust.ac.ir) (M. Asghari).

<https://doi.org/10.1016/j.seppur.2023.123399>

Received 14 November 2022; Received in revised form 29 January 2023; Accepted 8 February 2023

Available online 11 February 2023

1383-5866/© 2023 Elsevier B.V. All rights reserved.

[11] and inorganic pollutants [12] from water and wastewater. Biochar has been widely promoted as an advantageous alternative technology for metal elimination in water and wastewater treatment [13]. Mohan et al. [14] calculated the elimination yields of lead (Pb) and cadmium (Cd) ions using oak bark char which are similar to those for Calgon F-400 (commercial type of activated carbon). The obtained results of research by Chen et al. [15] illustrated that biochar made from corn straw and wood are good candidates for absorption of zinc (Zn) and copper (Cu) from water solutions. In using soybean stalk biochar, Kong et al. [16] reported 75–87 % mercury removal in aqueous solutions. These examples have indicated the advantageous elimination of different heavy metals by biochar prepared from a diversity of feedstock.

In addition, biochar can be engineered and functionalized through surface modification as well as pretreatment of feed stocks [17], which can enhance its adsorption capacities for heavy metals which are analogous or even better than activated carbon. For example, Inyang et al. [18,19] used anaerobically digested biomass to prepare biochar which showed greater Pb adsorption capacity than activated carbon. Moreover, there are other modifications that can significantly improve the sorption capacity of biochar for metals (e.g., Cu) from aqueous phase. Physical treatment of the feedstock is one of these modifications in which pulverization is being used before pyrolysis [20].

Up to now, research has considered the adsorption of heavy metals on biochar derived from lignocellulosic biomass [21]. Cellulose, lignin, and hemicellulose are the major sources of materials for the production of biochar with high surface area and oxygen-rich functional groups [22]. These materials have shown high performance in removing different heavy metals [21]. Inyang and et al. displayed that the adsorption capacities of biochar prepared from wooden biomass could reach a biosorption capacity of 89,600 mg/kg for the heavy metals removal which is comparable to activated carbon [21,23]. In addition, heavy metals removal efficiency of the lignocellulosic biochar reached 21,840 mg/kg in wastewater stream from leather tanning and finishing industry [24], demonstrating biochar's agile performance under tough conditions. For a deeper understanding of this topic, most studies so far followed similar production process for biochar by pyrolysis at relatively high temperature. The capability of biochar for heavy metal biosorption in different operating conditions has been examined by varying initial metal concentration, adsorbent dosage and solution pH. Based on the results from experiments, isotherm models, adsorption kinetic models, and maximum adsorption capacity of the biochar were consequently defined. The biosorption mechanism may include ion exchange of heavy metals with cations such as  $Mg^{2+}$ ,  $K^+$ ,  $Na^+$  and  $Ca^{2+}$ , surface complexation, precipitation with minerals, and coordination with  $\pi$  electrons [25]. It should be noted that such experimental methods are highly valuable, but are relatively complicated and inefficient to unravel the adsorption mechanisms, relative contributions of different variables, and the effects of biochar characteristics (e.g., particle size, surface area) in biosorption. In addition to the characteristics of biochar, there are other influential factors such as initial pollutant concentration, metal properties and environmental conditions that directly affect the biosorption of heavy metals [21]. Furthermore, the common experimental approach typically involves examining control variables individually, which does not help to define the relative contributions of each influential factor to total biosorption capacity. It is imperative to develop a better understanding of the relative importance of each variable, which will provide more insight to the biosorption of heavy metals in real wastewater and improve the overall removal efficiency.

Heavy elements are among the most important environmental pollutants, which have been of great interest in the last few decades. Heavy metals are not biodegradable easily and therefore pose long-term threat to human health, through food, drinking water and air [26] as the most common exposure pathways to our body. Due to the harmful environmental effects of heavy metals on human health and environment, more studies should be done on the source, concentration and methods to prevent these pollutants from entering to the environment (water, soil

and air) [27].

Currently, machine learning (ML) methods as a popular modelling practice are widely researched for predicting the process performance in water and wastewater treatment [28]. However, the application of machine learning models in adsorption assessment is limited up to now, and this study was designed to address such a knowledge gap. Therefore, building and training a high-quality model which is able to provide accurate estimates regarding biosorption efficiency is the purpose of this study. In the current study, the ANFIS, CSA-LSSVM, PSO-ANFIS and GP models were expanded to estimate the biosorption capacity of 44 different biochar sorbents for the elimination of lead, copper, zinc, cadmium, arsenic and nickel. For the first time, novel and reliable machine learning models were applied to predict the biosorption capacity of biochar sorbents for the elimination of heavy metals. GP model yields an accurate and simple mathematical equation for the prediction of the adsorption process. This simple equation can be used by various researchers who do not have any knowledge about machine learning science. The reliability of models is authenticated by a simple MATLAB code and an instruction for the implantation of the code. The developed models are compared with previous studies. Appropriate statistical measures were used to validate the model's accuracy.

## 2. Theory

### 2.1. Least-squares version of the support vector machine model

Support Vector Machine (SVM) which works relying on the theory of statistical learning is considered a precise methodology in ML [29]. Due to high flexibility and limited number of tuning variables, SVM has been deliberated for regression analysis [30].

### 2.2. Adaptive neuro-fuzzy inference system

ANFIS is a constructing foundation for fuzzy inference system (FIS) which has irreplaceable and exceptional architecture. In this study, a particular adaptive network which is a primary architecture for FIS and the black-box model have been utilized to optimize and simulate the process. The input and output, preprocessor and database, fuzzifier, FIS, fuzzy system creator, defuzzification, and an ANN as the fuzzy system are the structural and fundamental elements of the developed model. Defuzzification is elaborated as a process to generate quantifiable results and acquire singular output from fuzzy set in fuzzy logic (FL). The learning algorithms of Sugeno fuzzy model have been employed and described in this section. Both FL and ANN form a fuzzy-neural network benefit from a five-layer architecture in the multi-layer network ANFIS structure. The simplicity of ANFIS architecture can be included as inputs  $x$  and  $y$ , and an output such as  $z$ . 'If-then' rules as a two-fuzzy rule embedded in a first-order Sugeno fuzzy model can be described as follows [31]:

Rule 1: If  $x_1$  is  $A_1$  and  $x_2$  is  $B_1$  etc.; then  $f_1 = p_1x_1 + q_1x_2 + \dots + r_1$ ;  
Rule 2: If  $x_2$  is  $A_2$  and  $x_2$  is  $B_2$  etc.; then  $f_2 = p_2x_1 + q_2x_2 + \dots + r_2$ ;

A five-layer feed forward network has been employed in the ANFIS structure. The functions utilized in each layer are represented in Eq. (1):

$$Q_{1,i} = \mu_{A_i}(m) \quad i = 1, 2 \quad (1)$$

The layer functions of input and output as a membership function (MF) are defined in Eqs. (1) and (2), respectively:

$$Q_{1,j} = \mu_{B_j}(m) \quad j = 1, 2 \quad (2)$$

where  $\mu$  is the membership function. Layer 2 (rule nodes) can be defined based on Eq. (3):

$$w_i = \mu_{A_i}(m) \mu_{B_j}(m) \quad (3)$$

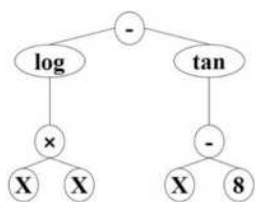


Fig. 1. Schematic of the GP tree of  $\log(X^2) - \tan(X-8)$ . Copyright 2021, Reproduced with permission from [33] Elsevier Science Ltd.

In layer 3 (normalized layer), the weight function can be normalized as in Eq. (4):

$$w_i = \frac{w_i}{w_1 + w_2}, i = 1, 2 \quad (4)$$

Layer 4 (consequent nodes) are expressed as the defuzzy layer by Eq. (5):

$$\bar{w}_i f_i = w_i (m p_i + n p_i + r_i) i = 1, 2 \quad (5)$$

Layer 5 rules from the last layer:

$$Q^5 = \sum_{i=1}^n \bar{w}_i f_i \quad (6)$$

The parameter set is defined by  $(p_i, q_i, r_i)$  and the output of layer is named by  $\bar{w}_i$ .

### 2.3. Genetic programming approach

In the GP method, the arrangement of the relationships (e.g. between dependent and independent parameters) has been postulated without any assumptions. An appropriate and firm relation, however, is established for any data set that embody in each of the three different logical categories. The first one is for those logically-expressed data while the second category is allocated for mathematical formats as a normal mathematical statement. Moreover, the third category is for completely unidentified assembly of mathematical functions. The two constituents of the GP implementation include (i) a parse tree, as a set of basic operators including “+, −, ×, ÷, log ...” that are RNA role mimics, and (ii) the core constituents of the functions along with the function-related parameters.

This system changes the generation of population to find well-performed solutions, and random population selection models are used to start the evolution process. The fitting values of each solution would be computed based on the dependent and independent variables. In ranking method, the selection of the models is performed according to the fitness values.

Crossover and mutation are the key parameters which will result in the “Children” or “offspring”. Crossover operators are commonly applied to preserve correspondent properties among generations, while the mutation operator would be used to transfer the populations randomly in the parse tree. The procedure then reaches the final stage at the main generation and constantly reiterates up to its termination [32]. The function “ $\log(X^2) - \tan(X - 8)$ ” is depicted schematically in Fig. 1.

Table 1

The properties of heavy metal ions studied for their removal using biochar.

Metal	Electronegativity [35]	Ionic radius (Å) [36]	MW
Cu <sup>2+</sup>	1.9	0.72	63.5
Zn <sup>2+</sup>	1.65	0.74	65.38
Pb <sup>2+</sup>	2.33	1.2	207.2
Cd <sup>2+</sup>	1.69	0.97	112.4
Ni <sup>2+</sup>	1.91	0.69	58.7
As <sup>3+</sup>	2.18	0.58	74.9

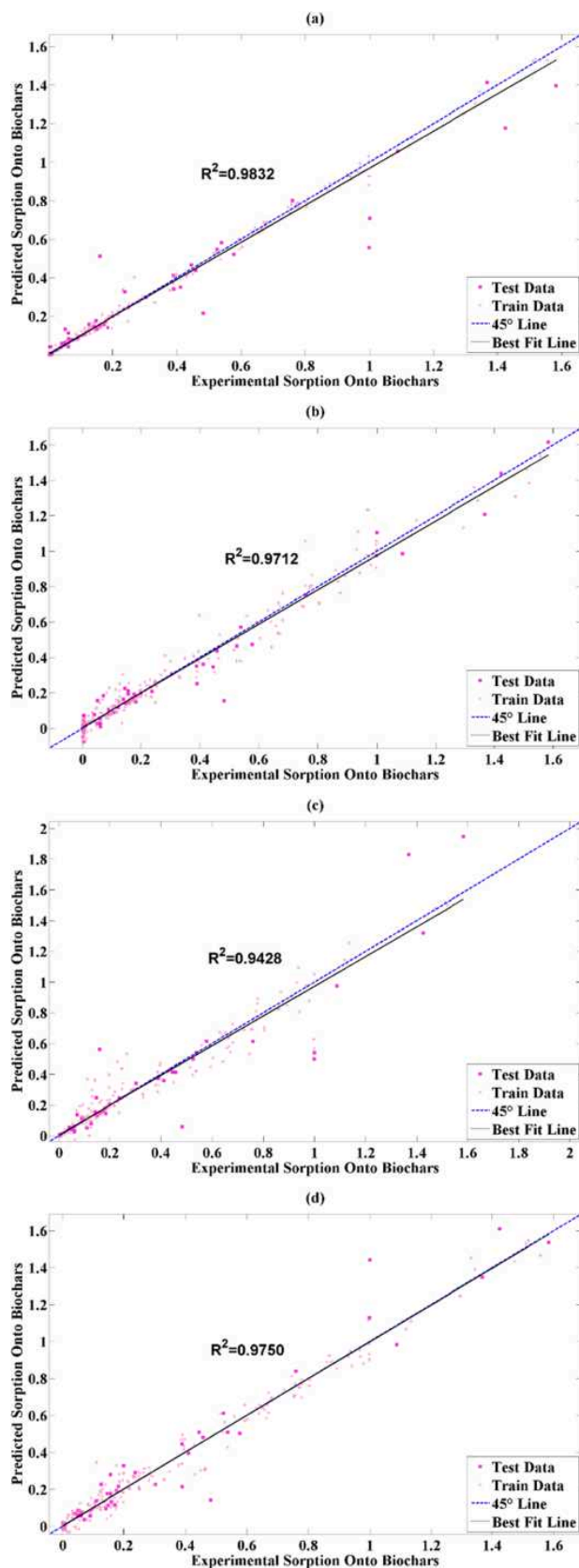


Fig. 2. Predicted vs experimental biosorption capability of biochar for heavy metals by a) LSSVM, b) PSO-ANFIS, c) ANFIS, and d) GP models.

### 3. Data collection

The 353 sets of experimental data regarding the biosorption of metal ions including Zn<sup>2+</sup>, Cu<sup>2+</sup>, Pb<sup>2+</sup>, Ni<sup>2+</sup>, Cd<sup>2+</sup> and As<sup>3+</sup> on biochar were selected from previous study [34] and other publications and its details are available in Table S1 in Supplementary material. The raw data were randomly split into the training (282) and testing (71) datasets. Beyond that, lignocellulosic biomass as the main constituent of the 44 selected biochar has been produced at temperature ranging between 300 °C and 700 °C. Sixteen important and influential factors were postulated to develop predictive models for estimating biochar adsorption capacity for heavy metals. These factors were grouped into four categories. The first one concerns the characteristics of biochar, such as biochar pH in water (pH<sub>H2O</sub>), biochar operating temperature in pyrolysis process (Tp), biochar surface area (SA, m<sup>2</sup>/g), ash content (ash, %), amount of total carbon in biochar (C, mass %), cation exchange capacity (CEC, cmol/kg), particle size of biochar (PS, mm), and molar ratio to carbon (O/C, H/C, (O + N)/C). The second one is the biosorption condition such as the water temperature (T, °C), and pH of solution (pH<sub>sol</sub>). The third one relates to the initial concentration ratio of heavy metals over biochar (C<sub>0</sub>, mmol/g). The fourth one concerns the characteristics of heavy metal such as the electronegativity (χ), radius of ions (r, nm), and molecular weights (MW) which are presented in Table 1.

### 4. Results and discussion

#### 4.1. Model development

Several kinds of ML methods such as LSSVM, Hybrid-ANFIS, PSO-ANFIS and GP were employed to predict the biosorption of heavy metals by biochar. No explicit methods or formulas have been presented in the literature to predict the necessary MF number [37]. Hence, the MF numbers should be determined by trial-and-error. The most accurate predictions were obtained from Gaussian type MF [38,39]. The characteristics of ANFIS (FCM) model with 18 rules was summarized in Table S2. The model training was set as 2000 epochs. An advanced ANFIS model coupled with a PSO algorithm [40] was expanded in this study to estimate the performance of heavy metal elimination using biochar. Having employed the PSO algorithm, the FCM type of ANFIS was trained followed by determining the optimal values of ANFIS parameters. Similarly, many parametric reports were used to define the optimal values of PSO parameters in order to support and enhance the PSO-ANFIS model development. Many studies applied the Gaussian type as MFs [41]. The details of PSO-ANFIS parameters were demonstrated in Table S3. The population size or number of individuals creating a population in each generation, number of generations to run, and maximum depth of trees were set at 1000, 300, and 7, respectively. Crossover and mutation have been chosen in this program. In the end, the superlative GP model after meeting the termination criterion was obtained:

$$\begin{aligned}
 \text{Biosorption capacity (mmol/g)} = & 0.03178 \sin(0.4795pH_{(sol)} + 0.3738C_0 - 0.4795H/C + \sin(pH_{(sol)} - T) - \sin(8.709H/C) + 0.3738\sin(pH_{(sol)} \\
 & - 3.485) - 0.03178(\sin(9.482\sin(0.6186pH_{(sol)}))\sin(pH_{(sol)})) - pH_{(sol)}\sin(\sin(\sin(C_0))) + 0.3051pH_{(sol)} + H/C \\
 & + \sin(0.6491pH_{(sol)}) + \sin(pH_{(sol)}\sin(0.6362pH_{(sol)})) + (1.125 \times 10^{-7})C_0((Ash \\
 & + \sin(pH_{(sol)})(C_0 - 9.678))(0.4795pH_{(sol)} + 0.4795H/C - \sin(9.478Ash)) + \sin(\sin(0.659pH_{(sol)}))(SA - \sin(pH_{(sol)})(T \\
 & - pH_{(sol)})))(CEC - 2C_0)((T - Ash)(Ash - pH_{(sol)} + 9.323) + C_0(SA - 0.4795) - 0.4795Tp(C_0 - 9.482)) + 0.05205
 \end{aligned}
 \tag{7}$$

By using the CSA algorithm for optimization, the superlative values of LSSVM algorithm including γ (704.7) and σ<sup>2</sup> (2.945156e + 04) were obtained using RBF kernel function.

#### 4.2. Testing and validation of the models

In order to simply predict the data using the methods developed in this study, we developed a MATLAB code. The instruction for running this code is available in the Supplementary information. Statistical and graphical methods were used for the evaluation of developed approaches. The cross-plot of predicted results vs the measured values using the graphical methods was presented for all models including ANFIS, PSO-ANFIS, LSSVM and GP. Fig. 2 presents the predicted values of the models versus actual values concerning the removal of heavy metals using biochar. The modeling results display that the estimated values of predictors and actual results are in good agreement, based on the values of correlation coefficient (R<sup>2</sup>).

The relative deviation of the output values from the experimentally determined values was calculated. As stated in Fig. 3, the results illustrated that the relative errors were very small for the modeling output from LSSVM, PSO-ANFIS and GP models. In comparison, relatively large errors were found for the output from ANFIS, mainly occurring when the low biosorption capacity was low. Therefore, LSSVM, PSO-ANFIS and GP models were recommended for further evaluation.

To show the preciseness of presented models, statistical parameters were used. Eqs. (8)-(11) present the mathematical calculations of these parameters:

$$R^2 = 1 - \frac{\sum_{i=1}^n [x_i^{predicted} - x_i^{experimental}]^2}{\sum_{i=1}^n [x_i^{predicted} - x_m]^2}, x_m = \frac{\sum_{i=1}^n x_i^{experimental}}{n}
 \tag{8}$$

$$AARD = \frac{1}{n} \sum_{i=1}^n \left| \frac{x_i^{predicted} - x_i^{experimental}}{x_i^{experimental}} \right|
 \tag{9}$$

$$MSE = \frac{1}{n} \sum_{i=1}^n (x_i^{experimental} - x_i^{predicted})^2
 \tag{10}$$

$$\text{Standard deviation (STD)} = \sqrt{\frac{\sum_{i=1}^n (x_i^{predicted} - x_m)^2}{n}}
 \tag{11}$$

The statistical data of the testing, training and total data sets are summarized in Table 2. The values of R<sup>2</sup> are all very high, which are equal to 0.9750 (GP), 0.9428 (ANFIS), 0.9712 (PSO-ANFIS) and 0.9832 (LSSVM) models, for the total data sets. In comparison, ANFIS presented the lowest R<sup>2</sup> values, especially for the test dataset (0.8796). The relative errors from modeling are very small, as shown by the MSE values, of which ANFIS generated the highest value (0.0069) compared to the other three models. This small margin of error indicates that the experimental data and estimations are in great agreement. In term of STD values, all four models presented very similar performance. On a positive note, ANFIS produced the lowest AARD value (0.21) among the four models. Overall, GP, PSO-ANFIS and LSSVM were demonstrated to

be effective models for the heavy metal biosorption process.

In order to better understand, the obtained results of this research were compared with the results of previous published articles, as

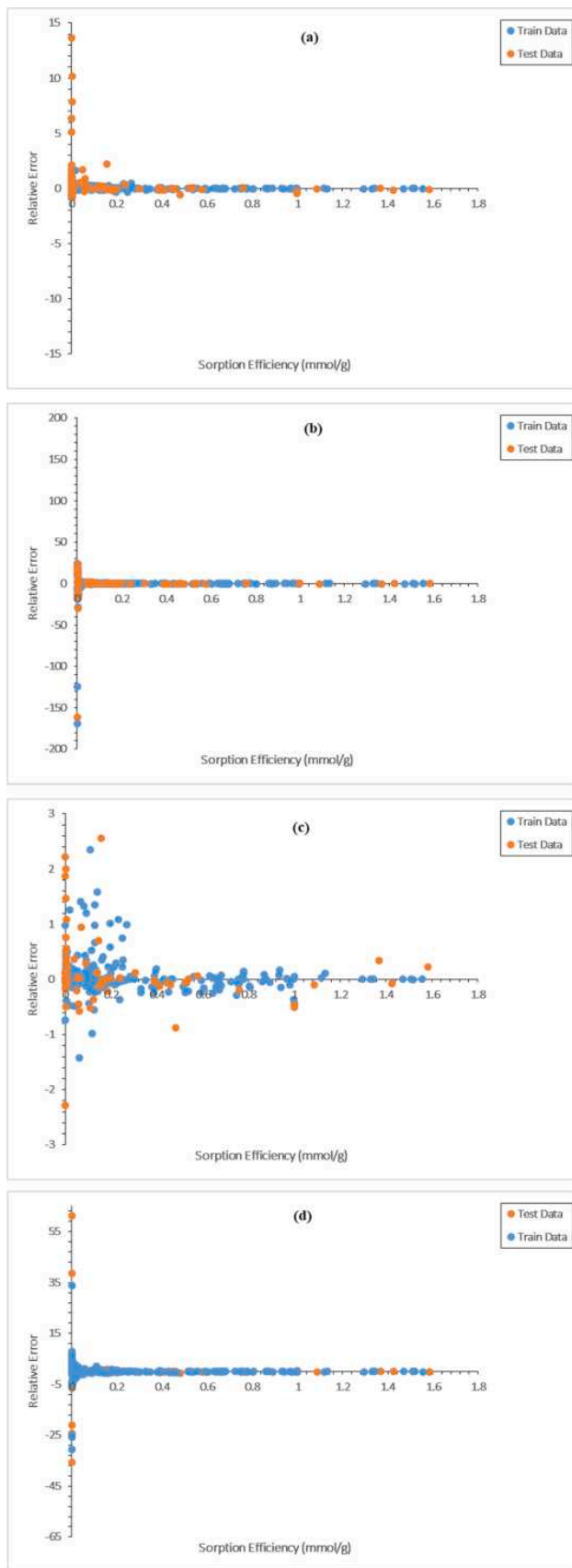


Fig. 3. Relative error deviation a) LSSVM, b) PSO-ANFIS, c) ANFIS, and d) GP models.

Table 2  
Accuracies of various ML models used in this study.

Parameter	Dataset	GP	ANFIS	PSO-ANFIS	LSSVM
R <sup>2</sup>	Train	0.9828	0.9633	0.9718	0.9969
	Test	0.9546	0.8796	0.9695	0.9400
	All	0.9750	0.9428	0.9712	0.9832
MSE	Train	0.0020	0.0042	0.0033	0.0004
	Test	0.0071	0.0173	0.0041	0.0087
	All	0.0030	0.0069	0.0034	0.0020
STD	Train	0.3368	0.3336	0.3366	0.3368
	Test	0.3871	0.3782	0.3510	0.3234
	All	0.3475	0.3432	0.3397	0.3343
AARD	Train	1.54	0.16	3.52	0.20
	Test	3.68	0.38	6.69	1.01
	All	1.97	0.21	4.15	0.36

presented in Table 3. According to Table 3, LSSVM model has a better R<sup>2</sup> than other models, which shows the high agreement between experimental data and predicted data. In addition, the presented results of GP model are acceptable with high accuracy. Also, the obtained mathematical model can unravel many works in this field and help researchers to choose better biochar materials.

4.3. Sensitivity analysis

The sensitivity analysis calculates the amount of variation in the output value in response to changes in the input value. The sensitivity analysis was used to investigate different aspects of the developed ML models. In order to obtain sensitivity analysis, the relevancy factor (r) for the biosorption of heavy metal ions on biochar was calculated by Eq. (12) [43]:

$$r = \frac{\sum_{i=1}^n (X_{k,i} - \bar{X}_k)(Y_i - \bar{Y})}{\sqrt{\sum_{i=1}^n (X_{k,i} - \bar{X}_k)^2 \sum_{i=1}^n (Y_i - \bar{Y})^2}} \tag{12}$$

where the average amount of output is displayed with “ $\bar{Y}$ ” while “ $Y_i$ ” is the value of output number I, “ $\bar{X}_k$ ” is the average amount of input number k, “ $X_{k,i}$ ” is the value of input number and “n” is the count of data sets.

The sensitivity analysis result can be obtained based on the experimental data. The r values are obtained in the range of -1 and +1. If r values are more than 0, it can be deduced the correspondent parameter has positive effect on the output of the process. If r values are less than 0, it can be deduced the correspondent parameter has negative effect on the output of the process. For example, in this study, the r value for particle size of biochar (PS, mm) is positive (0.448); hence, it can be concluded that by increasing the particle size of the biochar, the biosorption of heavy metal ions on biochar is increased. Also, this value (0.448) is higher than the r value for biochar operating temperature in pyrolysis process (Tp) at 0.0063. So, it can be deduced that PS has a higher impact than Tp on the biosorption of heavy metal ions on biochar.

The comparative importance of several parameters regarding the heavy metal biosorption is presented in Fig. 4. The outcomes

Table 3  
Comparison of performance between current models and previous models.

Model	R <sup>2</sup>	MSE	Reference
Kriging	0.980	0.0024	[42]
KELM	0.919	0.00008	[42]
ANN	0.948	0.0032	[34]
RF	0.973	0.0062	[34]
ANFIS	0.942	0.0069	This Work
CSA-LSSVM	0.983	0.0020	This Work
PSO-ANFIS	0.971	0.0034	This Work
GP	0.975	0.0030	This Work

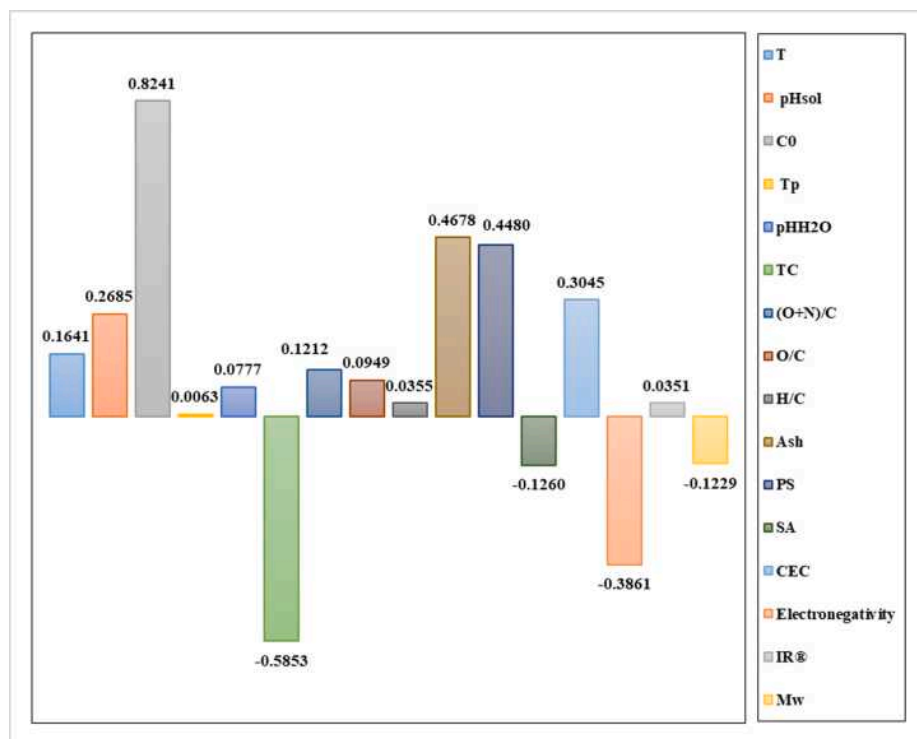


Fig. 4. Effect of input parameters on the prediction of biosorption capacity of biochar.

demonstrate that the biosorption of heavy metal ions on biochar is proportional to  $T_p$  (0.2 %),  $C_0$  (20 %),  $pH_{H_2O}$  (1.9 %), H/C (0.9 %), PS (11 %), CEC (7.5 %),  $pH_{sol}$  (6.6 %), T (4 %), Ash (11.5 %), (O + N)/C (3 %),  $r$  (0.9 %) and O/C (2.3 %). On the other hand, biosorption is inversely proportional to SA (−3.1 %), MW (−3%), C (−14.4 %) and  $\chi$  (−9.5 %). Based on the analysis, the most and the least significant effects are attributed to the variables  $C_0$  and  $T_p$  with relevancy factors of 0.86 and 0.02, respectively. Moreover, it is reported that the initial concentration of heavy metals has a considerable effect on the biosorption performance [44]. This is likely due to the fact that when the concentration of heavy metal ions is low, the biosorption of heavy metals mainly occurs on biochar surface. Since the core structure of the biochar and the heavy metal ions play important roles in their interactions, the biosorption capacity will increase with the increase in the heavy metal concentrations [45].

In addition, the comparative contributions of CEC can be attributed to the type of ions and nature of ion exchange process (e.g.,  $Na^+$ ,  $K^+$ ,  $Mg^{2+}$  and  $Ca^{2+}$ ) as well as the surface functional groups (e.g. carboxyl, carbonyl, phenolic) on biochar [23,24]. The results are consistent with the CEC and  $pH_{H_2O}$  data. Furthermore, the way that oxygen-containing functional groups along with the aromatic structures in biochar affect its biosorption process can be defined by the molar ratios such as (O + N)/C and H/C [46].

By increasing pH in solution, functional groups on the surface of biochar release their protons, therefore, it is probable for biochar to generate more negative charges and hence to increase its biosorption capacity for heavy metal cations. Additionally, the alkaline solutions [47] could derive in the precipitation of heavy metal cations. Considering the effect of several parameters, it was concluded that total carbon indicated negative effect on biosorption process which could be associated with the limited functional groups on the biochar surface. In case of electronegativity, no general trend was observed regarding its effect on the biosorption of heavy metals on biochar, similar to that reported by Park et al. [48].

## 5. Conclusions

Water pollution with heavy metals is one of the most important environmental problems that affects the life and health of people by causing serious diseases. Therefore, it is necessary to control their presence in the environment. In this study, ML models of ANFIS, LSSVM, PSO-ANFIS, and GP were developed as valuable algorithms to effectively predict biochar elimination of heavy metal ions in water and wastewater. Based on the comparison between the predicted and experimental results, all four models presented satisfactory performance in simulating the biosorption of heavy metals by biochar. Presented results of this research, had better performance than other published papers. Using statistical analysis, it is concluded that the LSSVM, PSO-ANFIS and GP models showed better performance than ANFIS model, due to their high  $R^2$  values and low MSE values. The most influential variables are found to be initial metal/biochar concentration ratio and total carbon content in biochar.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

Data will be made available on request.

## Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.seppur.2023.123399>.

## References

- [1] J.E. Amonette, S. Joseph, Characteristics of biochar: microchemical properties. In: Biochar for Environmental Management, Routledge, 2012, pp. 65-84.

- [2] D. Laird, P. Fleming, B. Wang, R. Horton, D. Karlen, Biochar impact on nutrient leaching from a Midwestern agricultural soil, *Geoderma* 158 (2010) 436–442.
- [3] J.L. Field, C.M. Keske, G.L. Birch, M.W. DeFoort, M.F. Cotrufo, Distributed biochar and bioenergy coproduction: a regionally specific case study of environmental benefits and economic impacts, *GCB Bioenergy* 5 (2013) 177–191.
- [4] D. Mohan, A. Sarswat, Y.S. Ok, C.U. Pittman Jr, Organic and inorganic contaminants removal from water with biochar, a renewable, low cost and sustainable adsorbent—a critical review, *Bioresour. Technol.* 160 (2014) 191–202.
- [5] S. Tang, N. Shao, C. Zheng, F. Yan, Z. Zhang, Amino-functionalized sewage sludge-derived biochar as sustainable efficient adsorbent for Cu (II) removal, *Waste Manage.* 90 (2019) 17–28.
- [6] A. Ahmadvour, Using of activated carbon adsorption in wastewater industries, *J. Chem. Lett.* 3 (2022) 2–9.
- [7] A.A. Bukhari, Investigation of the electro-coagulation treatment process for the removal of total suspended solids and turbidity from municipal wastewater, *Bioresour. Technol.* 99 (2008) 914–921.
- [8] V. Verma, S. Tewari, J. Rai, Ion exchange during heavy metal bio-sorption from aqueous solution by dried biomass of macrophytes, *Bioresour. Technol.* 99 (2008) 1932–1938.
- [9] N.N.R. Ahmad, W.L. Ang, Y.H. Teow, A.W. Mohammad, N. Hilal, Nanofiltration membrane processes for water recycling, reuse and product recovery within various industries: a review, *J. Chem. Environ.* 45 (2022), 102478.
- [10] D. Kailash, P. Dharmendra, V. Anil, Low cost adsorbents for heavy metal removal from wastewater: a review, *Res. J. Chem. Environ.* 14 (2010) 100–103.
- [11] M. Inyang, B. Gao, A. Zimmerman, Y. Zhou, X. Cao, Sorption and cosorption of lead and sulfapyridine on carbon nanotube-modified biochars, *Environ. Sci. Pollut. Res.* 22 (2015) 1868–1876.
- [12] J. Meng, X. Feng, Z. Dai, X. Liu, J. Wu, J. Xu, Adsorption characteristics of Cu (II) from aqueous solution onto biochar derived from swine manure, *Environ. Sci. Pollut. Res.* 21 (2014) 7035–7046.
- [13] H.K.S. Panahi, M. Dehghani, Y.S. Ok, A.-S. Nizami, B. Khoshnevisan, S.I. Mussatto, M. Aghbashlo, M. Tabatabaei, S.S. Lam, A comprehensive review of engineered biochar: production, characteristics, and environmental applications, *J. Cleaner Prod.* 270 (2020), 122462.
- [14] D. Mohan, C.U. Pittman Jr, M. Bricka, F. Smith, B. Yancey, J. Mohammad, P. H. Steele, M.F. Alexandre-Franco, V. Gómez-Serrano, H. Gong, Sorption of arsenic, cadmium, and lead by chars produced from fast pyrolysis of wood and bark during bio-oil production, *J. Colloid Int. Sci.* 310 (2007) 57–73.
- [15] X. Chen, G. Chen, L. Chen, Y. Chen, J. Lehmann, M.B. McBride, A.G. Hay, Adsorption of copper and zinc by biochars produced from pyrolysis of hardwood and corn straw in aqueous solution, *Bioresour. Technol.* 102 (2011) 8877–8884.
- [16] H. Kong, J. He, Y. Gao, H. Wu, X. Zhu, Cosorption of phenanthrene and mercury (II) from aqueous solution by soybean stalk-based biochar, *J. Agric. Food Chem.* 59 (2011) 12116–12123.
- [17] P. Khare, A comprehensive evaluation of inherent properties and applications of nano-biochar prepared from different methods and feedstocks, *J. Cleaner Prod.* 320 (2021), 128759.
- [18] M. Inyang, B. Gao, Y. Yao, Y. Xue, A.R. Zimmerman, P. Pullammanappallil, X. Cao, Removal of heavy metals from aqueous solution by biochars derived from anaerobically digested biomass, *Bioresour. Technol.* 110 (2012) 50–56.
- [19] M. Inyang, B. Gao, W. Ding, P. Pullammanappallil, A.R. Zimmerman, X. Cao, Enhanced lead sorption by biochar derived from anaerobically digested sugarcane bagasse, *Sep. Sci. Technol.* 46 (2011) 1950–1956.
- [20] X.-J. Tong, J.-Y. Li, J.-H. Yuan, R.-K. Xu, Adsorption of Cu (II) by biochars generated from three crop straws, *Chem. Eng. J.* 172 (2011) 828–834.
- [21] S.M. Shaheen, N.K. Niazi, N.E. Hassan, I. Bibi, H. Wang, D.C. Tsang, Y.S. Ok, N. Bolan, J. Rinklebe, Wood-based biochar for the removal of potentially toxic elements in water and wastewater: a critical review, *Int. Mater. Rev.* 64 (2019) 216–247.
- [22] V. Dhyani, T. Bhaskar, A comprehensive review on the pyrolysis of lignocellulosic biomass, *Renew. Energy* 129 (2018) 695–716.
- [23] M.I. Inyang, B. Gao, Y. Yao, Y. Xue, A. Zimmerman, A. Mosa, P. Pullammanappallil, Y.S. Ok, X. Cao, A review of biochar as a low-cost adsorbent for aqueous heavy metal removal, *Crit. Rev. Environ. Sci. Technol.* 46 (2016) 406–433.
- [24] T.M. Abdel-Fattah, M.E. Mahmoud, S.B. Ahmed, M.D. Huff, J.W. Lee, S. Kumar, Biochar from woody biomass for removing metal contaminants and carbon sequestration, *J. Ind. Eng. Chem.* 22 (2015) 103–109.
- [25] Z. Wang, G. Liu, H. Zheng, F. Li, H.H. Ngo, W. Guo, C. Liu, L. Chen, B. Xing, Investigating the mechanisms of biochar's removal of lead from solution, *Bioresour. Technol.* 177 (2015) 308–317.
- [26] Z. Fu, S. Xi, The effects of heavy metals on human metabolism, *Toxicol. Mech. Methods* 30 (2020) 167–176.
- [27] M. Jamshaid, A.A. Khan, K. Ahmed, M. Saleem, Heavy metal in drinking water its effect on human health and its treatment techniques—a review, *Int. J. Biosci* 12 (2018) 223–240.
- [28] X. Zhu, D.C. Tsang, L. Wang, Z. Su, D. Hou, L. Li, J. Shang, Machine learning exploration of the critical factors for CO<sub>2</sub> adsorption capacity on porous carbon materials at different pressures, *J. Cleaner Prod.* 273 (2020), 122915.
- [29] L. Zhang, B. Chao, X. Zhang, Modeling and optimization of microbial lipid fermentation from cellulosic ethanol wastewater by *Rhodotorula glutinis* based on the support vector machine, *Bioresour. Technol.* 301 (2020), 122781.
- [30] A. Shokrollahi, A. Tatar, H. Safari, On accurate determination of PVT properties in crude oil systems: committee machine intelligent system modeling approach, *J. Taiwan Inst. Chem. Eng.* 55 (2015) 17–26.
- [31] A. Kamari, A. Safiri, A.H. Mohammadi, Compositional model for estimating asphaltene precipitation conditions in live reservoir oil systems, *JST* 36 (2015) 301–309.
- [32] M.A. Ghorbani, R. Khatibi, A. Aytek, O. Makarynsky, J. Shiri, Sea water level forecasting using genetic programming and comparing the performance with artificial neural networks, *Comput. Geosci.* 36 (2010) 620–627.
- [33] A. Dashti, A.S. Noushabadi, J. Asadi, M. Raji, A.G. Chofreh, J.J. Klemes, A. H. Mohammadi, Review of higher heating value of municipal solid waste based on analysis and smart modelling, *Renew. Sustain. Energy Rev.* 151 (2021), 111591.
- [34] X. Zhu, X. Wang, Y.S. Ok, The application of machine learning methods for prediction of metal sorption onto biochars, *J. Hazard. Mater.* 378 (2019), 120727.
- [35] A.L. Allred, Electronegativity values from thermochemical data, *J. Inorg. Nucl. Chem.* 17 (1961) 215–221.
- [36] R.T. Shannon, C.T. Prewitt, Effective ionic radii in oxides and fluorides, *Acta Crystallogr. Sect. B: Struct. Crystallogr. Cryst. Chem.* 25 (1969) 925–946.
- [37] M. Rezakazemi, A. Ghafarinazari, S. Shirazian, A. Khoshsima, Numerical modeling and optimization of wastewater treatment using porous polymeric membranes, *Polym. Eng. Sci.* 53 (2013) 1272–1278.
- [38] A. Dashti, M. Bazdar, E. Akbari Fakhradadi, A.H. Mohammadi, Modeling of catalytic CO<sub>2</sub> methanation using smart computational schemes, *Chem. Eng. Technol.* 45 (2022) 135–143.
- [39] M. Raji, A. Dashti, M.S. Alivand, M. Asghari, Novel prosperous computational estimations for greenhouse gas adsorptive control by zeolites using machine learning methods, *J. Environ. Manage.* 307 (2022), 114478.
- [40] P. Coulibaly, C.K. Baldwin, Nonstationary hydrological time series forecasting using nonlinear dynamic methods, *J. Hydrol.* 307 (2005) 164–174.
- [41] A. Tatar, A. Barati, A. Yarahmadi, A. Najafi, M. Lee, A. Bahadori, Prediction of carbon dioxide solubility in aqueous mixture of methyldiethanolamine and N-methylpyrrolidone using intelligent models, *Int. J. Greenhouse Gas Control* 47 (2016) 122–136.
- [42] Y. Zhao, Y. Li, D. Fan, J. Song, F. Yang, Application of kernel extreme learning machine and Kriging model in prediction of heavy metals removal by biochar, *Bioresour. Technol.* 329 (2021), 124876.
- [43] M. Hosseinzadeh, A. Hemmati-Sarapardeh, Toward a predictive model for estimating viscosity of ternary mixtures containing ionic liquids, *J. Mol. Liq.* 200 (2014) 340–348.
- [44] N. Zhou, H. Chen, J. Xi, D. Yao, Z. Zhou, Y. Tian, X. Lu, Biochars with excellent Pb (II) adsorption property produced from fresh and dehydrated banana peels via hydrothermal carbonization, *Bioresour. Technol.* 232 (2017) 204–210.
- [45] D. Mohan, C.U. Pittman Jr, Arsenic removal from water/wastewater using adsorbents—a critical review, *J. Hazard. Mater.* 142 (2007) 1–53.
- [46] M.S. Alam, D. Gorman-Lewis, N. Chen, S.L. Flynn, Y.S. Ok, K.O. Konhauser, D. S. Alessi, Thermodynamic analysis of nickel (II) and zinc (II) adsorption to biochar, *Environ. sci. technol.* 52 (2018) 6246–6255.
- [47] Z. Liu, F.-S. Zhang, J. Wu, Characterization and application of chars produced from pinewood pyrolysis and hydrothermal treatment, *Fuel* 89 (2010) 510–514.
- [48] J.-H. Park, Y.S. Ok, S.-H. Kim, J.-S. Cho, J.-S. Heo, R.D. Delaune, D.-C. Seo, Competitive adsorption of heavy metals onto sesame straw biochar in aqueous solutions, *Chemosphere* 142 (2016) 77–83.