Ethanol mediated As(III) adsorption onto Zn-loaded pinecone biochar: Experimental investigation, modeling, and optimization using hybrid artificial neural network-genetic algorithm approach

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ABSTRACT

Organic matters (OMs) and their oxidization products often influence the fate and transport of heavy metals in the subsurface aqueous systems through interaction with the mineral surfaces. This study investigates the ethanol (EtOH)-mediated As(III) adsorption onto Zn-loaded pinecone (PC) biochar through batch experiments conducted under Box–Behnken design. The effect of EtOH on As(III) adsorption mechanism was quantitatively elucidated by fitting the experimental data using artificial neural network and quadratic modeling approaches. The quadratic model could describe the limiting nature of EtOH and pH on As(III) adsorption, whereas neural network revealed the stronger influence of EtOH (64.5%) followed by pH (20.75%) and As(III) concentration (14.75%) on the adsorption phenomena. Besides, the interaction among process variables indicated that EtOH enhances As(III) adsorption over a pH range of 2 to 7, possibly due to facilitation of ligand–metal(Zn) binding complexation mechanism. Eventually, hybrid response surface model–genetic algorithm (RSM–GA) approach predicted a better optimal solution than RSM, i.e., the adsorptive removal of As(III) (10.47 μg/g) is facilitated at 30.22 mg C/L of EtOH with initial As(III) concentration of 196.77 μg/L at pH 5.8. The implication of this investigation might help in understanding the application of biochar for removal of various As(III) species in the presence of OM.

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Introduction

The presence of Arsenic (As) in the aquatic environment results in various health effects throughout the world, especially in the Asia pacific countries (Mandal and Suzuki, 2002; Smedley and Kinniburgh, 2002). Most reported As problems found in groundwater is predominantly caused by natural processes such as mineral weathering and dissolution resulting from a change in the geo-chemical environment when subjected to a reduced condition (Astrup et al., 2000; Namasivayam and Senthilkumar, 1998). On the other hand, As contamination is also caused by anthropogenic activities such as mining wastes,
petroleum refining, sewage sludge, agricultural chemicals, ceramic manufacturing industries and coal fly ash (Grossl et al., 1997; Viraraghavan et al., 1992; Podder and Majumder, 2016). In natural and waste water sources, As mainly exists in inorganic form, viz. trivalent arsenic, As(III) or pentavalent arsenate, As(V). Over a range of pH, As(III) is more toxic, mobile, and challenging to be scavenged from aqueous environment when compared to As(V) (Podder and Majumder, 2016). Similarly, natural organic matter (NOM) is formed in both terrestrial and aquatic environment through the chemical and microbial decomposition of terrestrial and aquatic animals and plants. About 20% of dissolved organic matter consists of carbohydrates, carboxylic acids, amino acids, hydrocarbons, and other organic acids (Wang and Mulligan, 2006). The decomposition of these structures may possess various combinations of functional groups, including esters, quinones, amino, nitroso, carboxylic, phenolic, and alcoholic hydroxyl, and other moieties (Perdue et al., 1980; Wang and Mulligan, 2006). These functional groups have different dissociation constants and deprotonate at different pH conditions. Few studies have reported the effects of mineral characteristics on the simultaneous sorption of arsenic and organic matter (Lin and Puls, 2000; Saada et al., 2003; Buschmann et al., 2006; Zhang et al., 2007; Tang et al., 2010; Liu et al., 2011; Shojaeimehr et al., 2013).

The presence of organic matters (OMs) and its oxidation products may result in the release of As mainly through the competition for available adsorption sites forming aqueous complexes, and changing the redox chemistry of site surface and arsenic species. In contrast, the organic compounds could also reduce the mobility of As by serving as a binding agent with saturation of metal cations (Wang and Mulligan, 2006). This information is useful to understand the fate and transport of As in the environment and provide information for As remediation technologies. The methylated metabolites of As such as monomethyl arsenic acid (MMAA), dimethylarsinic acid (DMAA) and dimethyl arsinoyl ethanol (DMAE), in which the inorganic As compounds methylated by microorganisms arise under oxidizing conditions (Wang and Mulligan, 2006). This condition comes into picture when the natural water is impacted by industrial pollution (Smedley and Kinniburgh, 2002; Terlecka, 2005). The environmental exposure of inorganic arsenic species to various natural and industrial organic pollutants, viz. oxidation products of OM and acetone, ethanol, methanol etc. may also influence its fate and transport in aquatic environment. Besides, the toxicity of arsenic is also highly dependent on its oxidation state and chemical composition (Wang and Mulligan, 2006; Podder and Majumder, 2016). Recent studies have shown that the methylated forms of inorganic arsenic (e.g., MMAA, DMAA, and DMEA) are highly cytotoxic, genotoxic, and potent inhibitor of some enzymes of human and animal cell types (Bao and Shi, 2010). However, little is known about the role of oxidation products of OMs (viz. ethanol, methane, and various organic acids) on the fate and transport of As in the water environment.

In the recent studies, some metal oxides such as Fe-loaded (Deschamps et al., 2005; Weng et al., 2009; Müñiz et al., 2009; Ghazizadeh et al., 2010), Zn-loaded (Yang et al., 2010; Vinh et al., 2015) and nano-structured sorbents (Deedar et al., 2009; Yang et al., 2010; Malana et al., 2011; Zheng et al., 2012) showed high affinity for arsenic species.

This study aims at investigating the potential of a metal (Zn) oxide loaded pine cone biochar for adsorptive removal of As(III) in the presence of ethanol in aqueous solution. Advanced machine learning approaches, viz. artificial neural network and genetic algorithm were used to elucidate the As(III) removal behavior in the presence of ethanol in aqueous environment. The combination of ANN and regression technique has been used for prediction of synergistic/antagonistic behavior among process variables (Paliwal and Kumar, 2009; Behera et al., 2012; Soleimani et al., 2013; Mahanty et al., 2013). Recently, genetic algorithm (GA) has also been recognized as a global optimization technique and found to be very useful when interfacing with response surfaces (Álvarez et al., 2009). GA has been demonstrated as an efficient technique that deals with single-response, multi-response and multi-constraint optimization problems (Álvarez et al., 2009). Thus, the main objectives of this research work are: (1) to investigate the influence of ethanol on As(III) removal by adsorption onto raw and Zn-loaded PC biochar at different pH, adsorbent and adsorbate doses, (2) to investigate the synergistic/antagonistic behavior of As(III) species with ethanol at different pH through regression and neural network modeling using the experimental data derived through Box-Behnken design, and (3) to determine the optimum concentrations of process variables for enhanced As(III) adsorption onto Zn-loaded PC biochar using hybrid response surface model–genetic algorithm (RSM–GA) model.

1. Materials and methods

1.1. Chemicals, materials and characterization

All the chemical reagents used in this study were of reagent/analytical grade and obtained from Daegung Chemical Co. Ltd., Korea, Junsei Chemical Co. Ltd., Japan, and Sigma-Aldrich, USA. All the chemical stock solutions were prepared using deionized water and were stored at 4°C. Raw and Zn-loaded PC biochars were prepared based on the methodology reported elsewhere (Vinh et al., 2015).

1.2. Batch adsorption studies

Batch experiments were carried out in Erlenmeyer flasks with known amount of PC biochar. The pH of the solution was adjusted by using 0.1 mol/L HCl or NaOH. These flasks were placed on a thermostat shaker (25°C) stirred at 120 r/min. The effect of pH on As(III) adsorption capacity was examined in the absence and presence of ethanol (30 mg C/L) by varying the pH from 2 to 12 with adsorbent and adsorbate doses of 10 g/L and 100 μg/L, respectively. After a specified time, the suspension was filtered and analyzed for residual As(III) and ethanol concentrations using hydride generation atomic absorption spectrophotometry (AA240-2004,Varian, USA) and total organic carbon (TOC) analyzer (5000 A, Shimadzu, Japan), respectively. Each experiment was conducted in duplicate under identical conditions and the average values were reported. Separate experiments were also conducted to investigate the effect of adsorbates (raw and Zn-loaded PC biochar) varying from 50 μg/L to 200 μg/L and, the adsorbent
doses were varied from 0.2 to 2.0 g/L. The adsorption capacity, \( q \) (\( \mu g/g \)), was calculated as:

\[
q = \frac{(C_0 - C)V}{W}
\]

where, \( C_0 \) (\( \mu g/L \)) and \( C \) (\( \mu g/L \)) are the concentrations of adsorbate in the solution at time zero and any time 't', respectively, \( V \) (L) is the volume of solution, and \( W \) (g) is the mass of adsorbent.

1.3. Leaching studies

Based on the standard procedure (Kalembkiewicz and Sitarz-Palczak, 2015), leaching test was conducted to determine the stability of loaded Zn in PC biochar over a range of solution pH. The details of impregnation of Zn on PC biochar are available elsewhere (Vinh et al., 2015). The amount of Zn loaded is calculated by determining the concentration of Zn before and after the impregnation using hydride generation atomic absorption spectrophotometry (AA240-2004, Varian, USA). 1.0 g of Zn-loaded PC biochar in 100 mL aqueous solution (containing 30 mg C/L of ethanol) was agitated in an Erlenmeyer flask at 30 rpm and at 25°C for 24 hr. In order to determine the effect of solution pH on the leachability of Zn, the pH was adjusted to 2, 3, 4, 7, 10, and 12 using either 0.1 mol/L HCl or NaOH. After the specified time, leachate was filtered through a 0.45 \( \mu m \) filter paper and was analyzed. Each experiment was conducted in duplicate under identical conditions and the average values of % Zn release were calculated using Eq. (2) as follows:

\[
\% \text{ Zn-release} = \left( \frac{C_{ZnS} - C_{ZnPC}}{C_{ZnS}} \right) \times 100\%
\]

where, \( C_{ZnS} \) (mg/L) and \( C_{ZnPC} \) (mg/L) represent the concentration of Zn loaded on PC biochar during impregnation, and the concentration of Zn released during leaching test (after 24 hr), respectively.

1.4. Design of experiments, regression, and neural network modeling

In order to investigate the interaction effects of As(III) concentration, ethanol concentration, and pH on adsorption capacity, Box-Behnken design based batch experiments were conducted. The range and levels for these variables were coded according to Eq. (3), given in Table 1.

\[
X_i = \frac{x_i - x_0}{\Delta x}
\]

where, \( x_i \) and \( X_i \) are the coded and the real values of variables. \( x_0 \) and \( \Delta x \) are the center point of \( X_i \) and the step change in \( X_i \), respectively.

The synergistic and/or antagonistic interactions among these variables that influenced the As(III) adsorption capacity were represented by following quadratic polynomial equation (Eq. (4)) using RSM.

\[
Y = \beta_0 + \sum_{i=1}^{3} \beta_i X_i + \sum_{i=1}^{3} \beta_{ii} X_i^2 + \sum_{i,j=1, i \neq j}^{3} \beta_{ij} X_i X_j
\]

where, \( Y \) represented the As(III) response and \( \beta_i \), \( \beta_{ii} \), and \( \beta_{ij} \) are the coefficients of linear, square, and interactive effects of variables, respectively.

Next, an artificial intelligence based modeling technique, i.e., neural network (NN) was tested for modeling the adsorption process and for determining the effect of each process variable on adsorption capacity. A feed forward architecture (3-4-1) NN

<p>| Table 1 – Experimental design (Box–Behnken) for As(III) removal with experimental and predicted responses and its statistical validation. |</p>
<table>
<thead>
<tr>
<th>Exp. Number</th>
<th>As(III) (( \mu g/L ))</th>
<th>Ethanol (mg/L)</th>
<th>pH</th>
<th>As(III) adsorption capacity (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Experimental</td>
<td>Predicted (RSM)</td>
<td>Predicted (ANN)</td>
<td></td>
</tr>
<tr>
<td>1.</td>
<td>100</td>
<td>50</td>
<td>6</td>
<td>8.55</td>
</tr>
<tr>
<td>2.</td>
<td>200</td>
<td>10</td>
<td>6</td>
<td>10.25</td>
</tr>
<tr>
<td>3.</td>
<td>200</td>
<td>30</td>
<td>8</td>
<td>9.92</td>
</tr>
<tr>
<td>4.</td>
<td>150</td>
<td>30</td>
<td>6</td>
<td>9.44</td>
</tr>
<tr>
<td>5.</td>
<td>150</td>
<td>10</td>
<td>4</td>
<td>7.45</td>
</tr>
<tr>
<td>6.</td>
<td>150</td>
<td>30</td>
<td>6</td>
<td>9.28</td>
</tr>
<tr>
<td>7.</td>
<td>200</td>
<td>30</td>
<td>4</td>
<td>10.12</td>
</tr>
<tr>
<td>8.</td>
<td>150</td>
<td>10</td>
<td>8</td>
<td>9.30</td>
</tr>
<tr>
<td>9.</td>
<td>150</td>
<td>50</td>
<td>8</td>
<td>8.65</td>
</tr>
<tr>
<td>10.</td>
<td>150</td>
<td>30</td>
<td>6</td>
<td>9.41</td>
</tr>
<tr>
<td>11.</td>
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<td>4</td>
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</tr>
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<td>12.</td>
<td>200</td>
<td>50</td>
<td>6</td>
<td>9.69</td>
</tr>
<tr>
<td>13.</td>
<td>150</td>
<td>50</td>
<td>4</td>
<td>7.39</td>
</tr>
<tr>
<td>14.</td>
<td>150</td>
<td>10</td>
<td>6</td>
<td>6.81</td>
</tr>
<tr>
<td>15.</td>
<td>150</td>
<td>30</td>
<td>6</td>
<td>9.46</td>
</tr>
<tr>
<td>16.</td>
<td>150</td>
<td>30</td>
<td>6</td>
<td>9.29</td>
</tr>
<tr>
<td>17.</td>
<td>100</td>
<td>30</td>
<td>8</td>
<td>8.25</td>
</tr>
<tr>
<td></td>
<td>( R^2 )</td>
<td></td>
<td></td>
<td>0.92</td>
</tr>
<tr>
<td></td>
<td>RMSE</td>
<td></td>
<td></td>
<td>0.28</td>
</tr>
<tr>
<td></td>
<td>SEP</td>
<td></td>
<td></td>
<td>3.17</td>
</tr>
</tbody>
</table>

\( ^a \) Training data.

\( ^b \) Testing data.
model with back-propagation algorithm was used for training the batch experimental data. The details of NN criteria are given elsewhere (Mahanty et al., 2013). During training of network, sigmoidal function was used as the activation function for each neuron. Therefore, due to different measurement ranges of input/output variables and, to avoid saturation problems in the sigmoidal function, the model inputs/outputs were normalized and scaled in the rank of 0.1 to 0.9 using Eq. (5).

\[
X' = \frac{X - X_{\text{min}}}{X_{\text{max}} - X_{\text{min}}} + 0.1
\]  

(5)

where, \(X'\) is the normalized value of output variable \(X\) and \(X_{\text{min}}\) and \(X_{\text{max}}\) are their minimum and maximum values, respectively.

The connection weights of trained ANN models with the corresponding bias terms were used to estimate the relative importance of each process variable \((I_j)\) on As(III) adsorption capacity (\(\mu g/g\)) as given in Eq. (6).

\[
I_j = \sum_{k=1}^{m} \left( \left( \sum_{h=1}^{N_h} W_{jh}^h \right) \times W_{in}^{j0} \right) 
\]

(6)

where, \(N_i\) and \(N_h\) are the numbers of input and hidden neurons, respectively, \(W\) is the connection weights, the superscripts ‘i’, ‘h’ and ‘o’ refer to input, hidden and output layers, respectively, and the subscript ‘\(k\)’, ‘m’ and ‘n’ refer to input, hidden and output neuron respectively.

In order to evaluate the fitting and prediction accuracy of developed models, Root Mean Square Error (RMSE), and Standard Error of Prediction (SEP) were employed as given in Eqs. (7) and (8), respectively.

\[
\text{RMSE} = \sqrt{\frac{\sum_{i=1}^{n} (Y_{e,i} - Y_{p,i})^2}{n}}
\]

(7)

\[
\text{SEP(\%)} = \frac{\text{RMSE}}{Y_e} \times 100\%
\]

(8)

where \(Y_{e,i}\) is the experimental value of \(i\)th experiment, \(Y_{p,i}\) is the corresponding predicted value by model of \(i\)th experiment, \(Y_e\) is the mean value of As(III) adsorption capacity obtained from experimental data, and \(n\) is the number of the experiments.

1.5. GA optimization

Once the experimental data was fitted to quadratic model, the developed model was used as fitness function to optimize the concentration of interaction variables, viz. EtOH and As(III) over a range of \(pH\) using genetic algorithm. The aim of the optimization process was to find the three-dimensional optimal decision vector that contribute to the maximum As(III) removal in the presence of EtOH. Under stochastic search, genes (in the form of binary code 0 and 1) on chromosome, i.e., the real valued string represented the searching parameters. In this study, the chromosomes for the optimization process were consisted of three genes corresponding to searching parameters, such as As(III) concentration, EtOH concentration, and \(pH\). Each gene was represented by 20 bits of binary code, and hence each chromosome represented by 60 bits (Zafar et al., 2010). The optimization process was initialized with 50 randomly selected initial chromosomes. The genes of each chromosome were decoded as:

\[
X = D \left( \frac{X_{\text{max}} - X_{\text{min}}}{D_c} \right) + X_{\text{min}}
\]

(9)

\[
D_c = \sum_{i=1}^{bt} 2^{ni}
\]

(10)

where \(X\) represents the concentrations of As(III), EtOH, and \(pH\), bt is the bit length, \(D\) is decimal equivalence of binary digit, and \(D_c\) is the sum of all binary weights of each bit.

As shown in Fig. 1, the generated population of chromosomes was evaluated by employing a certain fitness function (in this case quadratic equation) to get the optimal solution.

**Fig. 1** – Flow diagram of modeling and optimization scheme illustrating As(III) removal in presence of ethanol.
for As(III) adsorption. The following principle steps were taken place during the optimization process:

(1) randomly generation of an initial population of chromosomes;
(2) decoding the genes, viz. As(III) concentration, EtOH concentration, and pH of all chromosomes;
(3) evaluation of model predicted values of Eq. (3) with respect to As(III) adsorption;
(4) determine the fitness of all chromosomes and obtain the maximum fitness value ($fit_{\text{max}}$);
(5) if $fit_{\text{max}} \leq fit_{\text{req}}$, then carry out the next genetic operation to generate a new chromosome population and go to step (1).

For each generation, the operator such as selection, recombination, and mutation are performed to give the optimal solution of maximum As(III) removal in presence of EtOH.

2. Results and discussion

2.1. Screening the effects of adsorbent dose, As(III) initial concentration, and pH

In screening process, the raw and Zn-loaded PC biochar dose was varied from 0.1 to 2.0 g/L to determine the adsorbent dose. As shown in Fig. 2, an increase in adsorption capacity was observed for both raw and Zn-loaded PC biochar in the presence or absence of EtOH when the adsorbent dose was varied from 0.1 to 1.5 g/L. Increase in adsorption capacity (11.5%) was observed in presence of EtOH when As(III) concentration of 30 mg C/L (Zn-loaded PC biochar: 9.7 μg/g; raw PC biochar: 8.7 μg/g). The As(III) adsorption on Zn-loaded PC biochar in the presence of EtOH might be through the following routes: (1) reaction of EtOH-Zn complexes on PC biochar (ligand exchange-surface complexation) with As(III) anions through metal-bridging mechanism, and (2) increase in affinity through As(III) speciation in aqueous solution (Zhang and Itoh, 2005). In contrast, As(III) adsorption on raw PC biochar (in presence of EtOH) was decreased by 18.18% (i.e., from 6.6 to 5.4 μg/g).

Fig. 3a and b represents the effect of initial concentration of As(III) on its adsorption on raw and Zn-loaded PC biochar, respectively, with EtOH concentration of 30 mg C/L. It was observed that the adsorption capacity was sharply increased within an hour followed by a gradual increase up to 6 hr before achieving the steady state. The As(III) adsorption capacity was increased with an increase in initial concentration of As(III) (in the range of 50–200 μg/L) with EtOH as a co-adsorbate. In equilibrium, the adsorption capacity of raw PC biochar were found to be 4.0, 4.6, 5.12 and 5.38 μg/g, while that of zinc-loaded PC biochar were 4.9, 8.5, 8.9 and 10.3 μg/g at an initial As(III) concentration of 10, 100, 150 and 200 μg/L. As(III), respectively. Maximum As(III) adsorption of 91.45% was observed at its initial concentration of 200 μg/L followed by a decrease of 84.78%, 73.82%, and 22.5% at As(III) concentrations of 100, 150, and 50 μg/L, respectively. An increase in As(III) adsorption capacity of 21.43% was observed on Zn-loaded PC biochar in presence of EtOH (i.e. 8.5 μg/g) based on the previously reported adsorption capacity of 7.0 μg/g without EtOH (Vinh et al., 2015). In contrast, a decline in adsorption capacity from 5.7 to 4.6 μg/g with and
without EtOH, respectively, was observed on raw PC biochar. Thus, it was presumed that EtOH might have occupied the sites of raw PC biochar or interfered with the adsorption of As(III) anions on solid surface. At the same time, the interaction of EtOH onto Zn-loaded PC biochar facilitated the As(III) binding through metal-bridging mechanisms (Lin and Puls, 2000; Redman et al., 2002; Awual et al., 2011). It was also observed that the initial EtOH concentration (30 mg C/L) was decreased by 26.67% in the beginning and became stable thereafter at all initial As(III) concentration (Vinh, 2013).

Initial pH plays an important role in the interaction of NOM and its oxidation products with As(III), and subsequently during its movement in the aquatic system (Wang and Mulligan, 2006). Fig. 4 shows the effect of solution pH on simultaneous adsorption of As(III) and EtOH onto raw and Zn-loaded PC biochars. On raw PC biochar, As(III) adsorption capacity was increased with increase in pH from 2.0 to 5.0 followed by a decrease with increase in pH from 5.0 to 12.0. A maximum adsorption capacity of 5.1 μg/g was obtained at the pH of 4.8. In contrast, Zn-loaded PC biochar exhibited significantly different trend for simultaneous adsorption of As(III) and EtOH resulting due to a complex interaction between the modified surface groups of biochar, and EtOH and different As(III) species at different pH. As(III) adsorption capacity clearly increased from pH 2.0 to 7.0 and achieved most effective adsorption of 8.5 μg/g in the pH range of 5.0 to 7.0, then slightly decreased in the alkaline pH range. It is important to mention that the speciation of As(III) is affected by the solution pH (ionic strength = 0.01 mol/L) (Choi et al., 2012). The uncharged form of As(III), i.e. arsenic acid (H₃AsO₃) is dominated at pH range 2.0 to 9.2 and arsenic acid (H₂AsO₃) is a predominant species. The metal oxide surface also becomes negatively charged at this pH range, resulting in electrostatic repulsion between As(III) and oxide surface (Choi et al., 2012).

The SEM images (Fig. 5) clearly show the surface of the Zn-loaded PC biochar before and after adsorption of As(III) in the presence of EtOH. The surface of adsorbent before adsorption is rough and highly porous (Fig. 5a). The approximate size of pore and voids is in the range of 5.38–10.49 μm. The morphological changes with respect to the size of pores and surface after adsorption of As(III) ions is shown in Fig. 5b. It was observed that the size of pores has become reduced after As(III) ion adsorption.

2.2. Leaching characteristics of Zn as a function of solution pH

The pH of a solution determines the surface charge of the PC biochar, degree of ionization and speciation of Zn in the solution. The binding forces between the charged Zn ions in the solution and the surface of PC biochar affected by ionic strength of the solution contribute to the release of Zn species. It can be observed that the concentration of released Zn in aqueous solution decreases with increasing alkalinity of the leaching solution (Fig. 6). High leachability (9.88% ± 0.35%) was observed in the pH range of 2 to 4 followed by a low (3.25%) and very low (1.67% ± 0.25%) leachability at pH 7 and pH > 10. The leaching trend of Zn indicates the dependence of the release of zinc on the dissociation of its various species and on the potential of binding on charged surface of PC biochar. As reported by Kalembkiewicz and Sitarz-Palczak (2015), Zn²⁺ is dominant in the solution at pH < 6. Above pH 6, Zn(OH)⁺ and ZnO forms are dominant which facilitate the binding of Zn to the surface of adsorbent which results in the reduction of its leachability in the aqueous solution. Besides, the presence of Et(OH) in aqueous solution also affects the concentration of soluble form of Zn and responsible for the decrease in leaching of Zn in aqueous solution. The solubility of heavy metals has been reported to be effectively reduced through the use of specific group of organic compounds, obtained either through chemical synthesis or isolated from natural substances (Kalembkiewicz and Sitarz-Palczak, 2015).

2.3. Modeling and optimization of As(III) adsorption capacity

Preliminary experimental results revealed the superiority of Zn-loaded PC biochar for As(III) adsorption in the aqueous solution both in the presence and absence of EtOH. Thus, the interaction effect of EtOH and As(III) over a pH range of 2 to 8 was investigated under statistical based Box–Behnken design (Table 1). The experimental data were fitted to a regression equation up to various orders of model interaction terms.
quadratic, special cubic, and full cubic). The model performance was assessed by Fisher’s test for analysis of variance (ANOVA) and is given in Table 2. The model ‘F’ value of 12.22 indicates that the model well represented the experimental data. The determination coefficient ($R^2$) value of 0.92 indicates that only 8% of the variability in response was not explained by the model. Similarly, the adj. $R^2$ value, which corrects the $R^2$ value with respect to sample size and number of models terms, was 87.32% suggesting moderate predictability of the experimental data. The regression coefficient obtained from the non-linear regression analysis between As(III) adsorption capacity and the process variables (viz. As(III) concentration, EtOH concentration, and pH) is represented by Eq. (11).

$$\text{As(III)}_{\text{Pred}} = -7.63034 + 0.05166X_1 + 2.52631X_1 - 0.00152X_1X_2 - 0.00057X_1X_2$$

It was found that As(III) concentration and pH had a strong positive linear effect on As(III) adsorption onto Zn-loaded PC biochar ($p < 0.0001$). Moreover, significant negative quadratic effects of EtOH ($p = 0.0161$) and pH ($p = 0.0223$) on As(III) adsorption capacity was reported. Finally, a significant negative interaction between As(III) and EtOH on As(III) adsorption capacity was noticed which indicated their competition for the adsorption site on Zn-loaded PC biochar. The negative second-order effects of EtOH and pH indicated that these variables act as limiting factor for As(III) adsorption. A three-dimensional response surface plot (Fig. 7) was generated using MATLAB 7.8.1 (The Mathworks Inc., MA, USA) which demonstrated the interaction between As(III) concentration, EtOH concentration, and pH during As(III) adsorption.

From Fig. 7a, it was clear that EtOH concentration of 30 mg C/L was favorable for As(III) adsorption even at the high As(III) concentration. However, further increase in EtOH concentration led to a fall in As(III) removal possibly by the competition for meso/μ pores in Zn-loaded PC biochar. Fig. 7b shows the interaction between As(III) and varying pH at a fixed EtOH concentration of 30 mg C/L. This result indicated that EtOH accelerated the availability of As(III) through its speciation over a wide range of pH (from acidic to alkaline). Subsequently, Fig. 7c shows the interaction effect of EtOH and pH over As(III) adsorption onto Zn-loaded PC biochar at a fixed As(III) concentration of 150 μg/L. The appearance of about 3/4th of the contour plot indicated that almost all favorable pH range (i.e., 5 to 7) was covered in this study. Within this pH range, the fixed EtOH concentration of ~30 mg C/L served as a catalyst and facilitated the As(III) adsorption by providing the suitable binding sites for different available As(III) species. It is considered that the presence of Et(OH) could accelerate the speciation rate of As(III) within a certain pH range (i.e. 5-7) and thereby provided the different forms of As(III) to Zn-loaded PC biochar. In addition, its direct interactions within meso/micro pores and with Zn on the surface of PC biochar could provide the additional sites for As(III) adsorption through metal bridging. Ligand exchange-surface complexation mechanism between the carboxyl/hydroxyl functional groups of organic matters and metal (e.g., Al, Fe, and Zn) oxide surface has been proposed as the phenomenon for the sorption of OMs (Gu et al., 1994; Wang and Mulligan, 2006; Liu et al., 2011; Buschmann et al., 2006; Weng et al., 2009). Functional groups such as carboxyl, hydroxyl,
and amino groups have the potential to form strong complexes with metal cations. This ligand exchange-surface complexation mechanism for organic matters to metal (hydr)-oxide surface is similar to the sorption mechanism of As(III) and As(IV) onto metal surface (Wang and Mulligan, 2006). Therefore, it is expected that they may compete with As(III)/As(IV) anions for adsorption to the solid surfaces. Similarly the formation of organic matter-metal complexes, e.g., (Et(OH)-O-Zn) may strongly bind with the As(III)/As(V) anions through the metal bridge mechanisms. As(III) is a potent electrophile that can react strongly with amino, hydroxyl, and sulfhydryl groups due to their nucleophillic properties (Wang and Mulligan, 2006).

Based on these facts and SEM morphology of Zn-loaded PC biochar, it is concluded that the dissociation of As(III) species play an important role in As(III) removal from aqueous solution through strong electrostatic force between charged biochar surface and its species. It is suggested that above site saturation on the surface of biochar (pHPZC = 4.03), zinc was increasingly complexed by the addition of hydroxyl groups leading to a gradual formation of Z(A)-ZnOH surface. Arsenic adsorption predominantly occurred through surface complexation reactions than by electrostatic interactions (Wang et al., 2008). In the presence of EtOH, adsorption of As(III) onto Zn-loaded PC biochar was significantly higher over a wide range of pH as compared to the absence of EtOH and also onto raw PC biochar (in the presence/absence of EtOH). The molecules possessing functional groups such as alcoholic-hydroxyl, carboxylic, esters, quinone and other moieties have different dissociation constants and thus deprotonate at different pH conditions. At low pH values, they are protonated and uncharged, but at neutral and higher pH values, they are dissociated and become negatively charged (Wang et al., 2008; Goswami et al., 2012). Hence, ethanol (possessing the hydroxyl group) can be dissociated and negatively charged over a neutral pH range which might further interact with Zn-loaded PC biochar surface through ligand exchange-surface complexation mechanism between hydroxy group of ethanol and metal (Zn) loaded PC biochar. The formation of EtOH-metal complexes may strongly bind As(III) anions through metal-bridging mechanism (Lin and Puls, 2000; Redman et al., 2002). It is noteworthy that anionic arsenic species (e.g., H₂AsO₅, H₂AsO₃, and AsO₄³⁻) dominated the system at pH > 2.3 (Wang et al., 2008). This phenomenon might have been responsible for an enhanced

![Table 2 – ANOVA of fitted model and estimated regression coefficients for As(III) removal onto Zn-loaded PC biochar.](image)

<table>
<thead>
<tr>
<th>Source</th>
<th>Coefficient</th>
<th>MS</th>
<th>F-value</th>
<th>p value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercept/model</td>
<td>-7.63034</td>
<td>1.93</td>
<td>12.22</td>
<td>0.0017</td>
</tr>
<tr>
<td>X₁</td>
<td>0.05166</td>
<td>10.50</td>
<td>66.47</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>X₂</td>
<td>0.20308</td>
<td>0.027</td>
<td>0.17</td>
<td>0.6897</td>
</tr>
<tr>
<td>X₃</td>
<td>2.52631</td>
<td>1.97</td>
<td>12.46</td>
<td>0.0096</td>
</tr>
<tr>
<td>X₁X₂</td>
<td>0.00002</td>
<td>0.015</td>
<td>0.096</td>
<td>0.7653</td>
</tr>
<tr>
<td>X₁X₃</td>
<td>0.00152</td>
<td>1.57</td>
<td>9.93</td>
<td>0.0161</td>
</tr>
<tr>
<td>X₁X₂X₃</td>
<td>-0.14147</td>
<td>1.35</td>
<td>8.53</td>
<td>0.0223</td>
</tr>
<tr>
<td>X₁X₂</td>
<td>0.00057</td>
<td>1.32</td>
<td>8.35</td>
<td>0.0233</td>
</tr>
<tr>
<td>X₁X₃</td>
<td>0.00312</td>
<td>0.39</td>
<td>2.47</td>
<td>0.1601</td>
</tr>
<tr>
<td>X₁X₂X₃</td>
<td>0.00374</td>
<td>0.090</td>
<td>0.57</td>
<td>0.4757</td>
</tr>
<tr>
<td>Residual</td>
<td>0.16</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

As(III) adsorption over a neutral pH in addition to adsorption of predominant neutral arsenic species at acidic pH (pHₚZC of Zn-loaded PC biochar = 4.03) (Vinh et al., 2015). About 97.33%
and 99.33% of initial EtOH concentration (30 mg C/L) participated in the ligand exchange-surface complexation and As(III) speciation (Vinh, 2013).

2.3.2. Artificial neural network modeling of ethanol influence on As(III) adsorption

For the ANN modeling, a feed-forward neural network trained by Levenberg-Marquardt back-propagation algorithm with one hidden layer was constructed. The inputs of the network were As(III) concentration, EtOH concentration, and pH whereas the output was the As(III) adsorption capacity. The number of nodes in the hidden layer was fixed to four, which was optimized in sequential training steps (data not shown). The primary goal of the training was to minimize the error function by searching a set of connection weight and bias values that produce outputs equal or close to the target value. The experimental data of Box-Behnken design were used to feed the constructed neural network and was divided into training (13) and testing (4) data sets. In this study, testing of trained neural network was conducted using 30% of the total data set obtained from the same experimental conditions.

The structure of the trained neural network was represented by weights and bias values of each layer (Table 3), which were determined after training and validation of the networks. The trained feed-forward ANN model correlating the inputs to the output response of network as:

$$\text{ANN}_{\text{As(III)}} = \text{purelin}(\text{act.LW}[3,2]) \ast \text{tansig}(\text{act.LW}[2,1])$$

$$\ast \text{purelin} \left( \text{act.LW}[1,1] \ast p + \text{act.b}[1] \right) + \text{act.b}[2])$$

$$\ast \text{act.b}[3])$$

(12)

where, act.LW[i,j], act.LW[1,1], and act.LW[3,2] represent the weights ($N_i, i = 1-4$, i.e., number of neurons) of input, hidden, and output layers, respectively, with the purelin and tansig transfer functions. Similarly, act.b[1], act.b[2], and act.b[3] represent bias in input, hidden, and output layers, respectively.

The model prediction efficiency of the quadratic equation and neural network was assessed on the basis of some statistical constants such as $R^2$, RMSE, and SE. The calculated $R^2$ value for the ANN model (0.95) was comparatively higher than the regression model (0.92). The RMSE and SEP of the regression model (0.28 and 3.17%) were comparatively larger than those for the ANN model (0.25 and 2.80%), indicating a comparatively better applicability of the latter one (Fig. 8). RSM can explain the effect of each main factor and the interaction (synergistic/antagonistic) between independent parameters on the response. ANN can be used to develop and simulate the process behavior in any form of non-linearity and can overcome the limitation of quadratic non-linear correlation assumed in RSM (Shojaeimehr et al., 2013). During ANN training, back propagation algorithm is used whereas least-square technique utilizes a prior formulated mathematical relationship in the regression model that explains the contribution of each input variable and their interaction effects. Though ANN is criticized for lacking interpretability of the complex network weights, few researchers have represented the input weights in terms of relative measures, viz. neural interpretation diagram, Garson’s algorithm, sensitivity analysis, and connection weight methods (Paliwal and Kumar, 2011). In this study, the connection weights of the fitted neural network were used to estimate the relative importance of each process variable, viz. As(III) concentration, EtOH concentration, and pH on As(III) adsorption capacity using Garson’s equation (Eq. (6)). It was observed that EtOH in aqueous solution has maximum relative importance of 64.5% on As(III) removal basically due to the interaction with the adsorption site. In contrast, pH and

<table>
<thead>
<tr>
<th>Topographic layer</th>
<th>Connection weights of neurons</th>
<th>Relative importance (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$N_1$</td>
<td>$N_2$</td>
</tr>
<tr>
<td>Input-hidden layer</td>
<td></td>
<td></td>
</tr>
<tr>
<td>As(III) concentration</td>
<td>2.0395</td>
<td>−0.1536</td>
</tr>
<tr>
<td>Ethanol concentration</td>
<td>0.0190</td>
<td>2.9864</td>
</tr>
<tr>
<td>pH</td>
<td>0.9894</td>
<td>−0.6693</td>
</tr>
<tr>
<td>Bias</td>
<td>0.2742</td>
<td>0.5483</td>
</tr>
<tr>
<td>Hidden-output layer</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Weights</td>
<td>−2.2633</td>
<td>0.6936</td>
</tr>
<tr>
<td>Bias</td>
<td>0.2430</td>
<td></td>
</tr>
</tbody>
</table>

Table 3 – Connection weights, bias and relative importance of each process variables on As(III) adsorption onto Zn-loaded PC biochar.

Fig. 8 – Graphical representation of maximum and average fitness function of As(III) adsorption capacity (μg/L) over 500 iterations of genetic algorithm (GA) optimization.
As(III) concentration influenced the As(III) removal by 20.75%, and 14.75%, respectively. However, in comparison to the neural network, regression analysis revealed the additional antagonistic interaction between As(III) and EtOH concentration at different solution pH. The linear regression coefficients of variables were equivalent to the relative importance of each factor derived from the connection weights and bias values. As predicted by ANN model, the impact of EtOH on As(III) adsorption was comparatively higher than the other two variables. Under regression modeling, it was observed that EtOH had a positive linear effect over a certain concentration. Besides, the increase in EtOH concentration resulted in a decrease in As(III) adsorption capacity. This decrease in adsorption occurred as a result of competition between As(III) and high concentration of EtOH (above 40 mg C/L) as shown in Fig. 7a. Hence, it was assumed that EtOH played a critical role during the removal of As(III) by PC biochar. The presence of OM and its derivatives might change the surface characteristics of the adsorbent and block the adsorption active sites (Wei et al., 2011; Zheng et al., 2012). However, as shown in Fig. 7a, the presence of EtOH in aqueous solution facilitated the removal of As(III) possibly due to ligand-metal surface complexation phenomenon.

### 2.3.3. Hybrid GA-RSM based optimization of ethanol influence of As(III) adsorption and experimental validation

GA is an efficient global optimization method having the ability to perform the parallel searches in the feasible space without the need of continuous, convex, or unimodal optimization function (Álvarez et al., 2009; Zafar et al., 2010). The GA-RSM based optimization process was initialized with ten randomly selected chromosomes. The fitness of each chromosome was evaluated by objective function (Eq. (11)) and the operators, viz. selection, recombination, and mutation were performed on the best chromosome of each generation to create a new population. This procedure was repeated until an optimized solution was achieved. The simulation of genetic optimization was performed with a maximum of 500 generations of GA to achieve maximum As(III) adsorption capacity in the given range of input variables. The maximum and average fitness is shown in Fig. 8. The different parameters of GA based optimization were set as: chromosome length (<em>k</em>cha) 30; population size (<em>N</em>pоп) 30; crossover probability (<em>P</em>c) 0.9; and mutation probability (<em>P</em>мут) 0.01 as reported elsewhere (Zafar et al., 2010). The hybrid RSM-GA approach predicted the maximum As(III) adsorption capacity of 10.47 μg/g at As(III) initial concentration of 196.77 μg/L, and 30.22 mg C/L of EtOH at a pH of 5.8 when adsorbed onto Zn-loaded PC biochar. In contrast, RSM predicted a maximum As(III) adsorption capacity of 10.51 μg/g at As(III) initial concentration of 198.47 μg/L, and 30.07 mg C/L at a pH of 6.9 when adsorbed onto Zn-loaded PC biochar. The validation in batch shake flask yielded the maximum As(III) adsorption capacity of 9.10 μg/g as the optimal solution given by RSM technique with a prediction error of 13.41%. On the other hand, validation of optimal solution by hybrid RSM-GA technique yielded a maximum As(III) adsorption capacity of 9.95 μg/g with a prediction error of 4.97%. Almost similar prediction of As(III) adsorption capacity was given by both the approaches with almost similar initial concentration of As(III) and EtOH, but at different pH. Furthermore, the experimental validation revealed the better predictability of hybrid RSM-GA approach toward As(III) adsorption onto Zn-loaded PC biochar (Table 4). The major difference between the RSM and hybrid RSM-GA approaches for the process optimization is the applicability of search algorithm. In RSM, desirability function approach is generally used to find optimal solution for response based on the constructed mathematical model (regression). In discriminant function analysis, the multi-criteria problem is reduced to a single problem of D optimization, i.e., the geometric mean of the measured dimensionless properties (δ) of each predicted response (Li et al., 2007). Because the scale of the desirability function (0 and 1) suggested the acceptability of responses, it may be confined to the local optimization region. However, GA, as an evolutionary algorithm, searches for the global optimization solution considering the function of three operators, viz. selection, crossing over, and mutation over modeled fitness function (quadratic function).

### 3. Conclusions

In the presence of EtOH, a significant enhancement (about 50%) in As(III) adsorption onto Zn-loaded PC biochar surface was observed. Further it was modeled and optimized using RSM and ANN, and hybrid RSM-GA approaches, respectively. The findings revealed that EtOH (at a concentration of 40 μg/L) could be able to facilitate the As(III) adsorption onto Zn-loaded PC biochar by systematic facilitation of ligand-metal (Zn) binding mechanism. Over a pH range of 2 to 7, an increase in As(III) adsorption was observed followed by a decrease due to electrostatic repulsion between predominant monovalent anionic species of As(III) and negative charged Zn-oxide surface of PC biochar. The predictive ability of the hybrid RSM-GA to find an optimal solution for maximum As(III) adsorption (10.47 μg/g) was excellent (prediction error = 4.97%). These findings provided a clue on the possible speciation of arsenic species (under the influence of EtOH), their adsorption and mobility in the natural subsurface aqueous system under a wide range of pH.

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**Table 4 – Optimal solution for As(III) adsorption onto Zn-loaded PC biochar predicted by RSM and hybrid RSM-GA along with validated results.**

<table>
<thead>
<tr>
<th>Optimization methodology</th>
<th>Process variable</th>
<th>Predicted response</th>
<th>Validated response</th>
<th>Prediction error</th>
</tr>
</thead>
<tbody>
<tr>
<td>RSM</td>
<td>As(III) [μg/L]</td>
<td>198.47</td>
<td>10.51</td>
<td>9.10</td>
</tr>
<tr>
<td>Hybrid RSM-GA</td>
<td>Ethanol (mg/L)</td>
<td>30.07</td>
<td>10.47</td>
<td>9.95</td>
</tr>
<tr>
<td></td>
<td>pH</td>
<td>6.9</td>
<td>5.8</td>
<td></td>
</tr>
</tbody>
</table>

Prediction error (PE) = (Experimental – Predicted) / Predicted × 100.
Acknowledgments

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References


