

# Application of Adsorbate Solid Solution Theory To Design Novel Adsorbents for Arsenic Removal Using CAMD

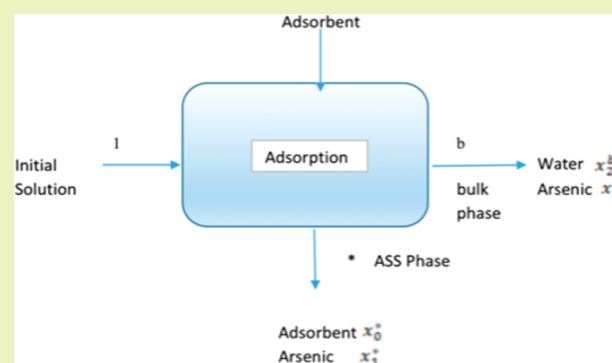
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**ABSTRACT:** Arsenic is a carcinogenic contaminant that pollutes the groundwater, a consequence of poor arsenic disposal. Various techniques are used to remove arsenic, such as oxidation, coagulation–flocculation, membrane filtration, ion exchange, and adsorption, among which adsorption is the most efficient method. Current arsenic separating agents on the market have a limited adsorption capacity. The overall objective of this work is to develop a computational tool for the design of novel adsorbents for arsenic remediation using clay materials including beidellite, zeolite, and sepiolite that are cheap and readily available. In the first part of this research, we use the group contribution method (GCM) to predict thermodynamic properties and calculate the UNIFAC interaction parameters between arsenic and other functional groups that are selected from clay materials. In the second part of this research, we utilize a computer-aided molecular design (CAMD) framework that develops new adsorbent candidates with enhanced adsorption capacities based on the group interaction parameters generated in the first part. The efficient ant colony optimization (EACO) algorithm maximizes the adsorption capacity with certain structural possibilities, thermodynamic property correlations, and process conditions. It was found that the newly designed adsorbents have an order of magnitude higher removal capacity than the adsorbents' reported in the literature.

**KEYWORDS:** Adsorbate solid solution theory, Arsenic removal, Group contribution method (GCM), Clay-based adsorbents, Computer-aided molecular design, Isotherm



## INTRODUCTION

The World Health Organization reports that there are at least 200,000,000 people at risk of arsenic poisoning from their drinking water due to the lack of both international regulations and cost-efficient removal solutions.<sup>1</sup> Even though arsenic contamination affects more than 70 countries, there has been no major global coalition to mitigate the arsenic outbreak. Unfortunately, efforts have fallen short when trying to come up with a universal filter for arsenic removal as there are very few filtration methods that have a high removal capacity, but there are even fewer filters that are also cost efficient.

Arsenic can be found in one of four oxidation states, and arsenate has an oxidation level of five.<sup>2</sup> Specifically, in drinking water, the most common form of arsenic is arsenate [As(V)]. Arsenate is either a salt or ester of the arsenic acid, and it is classified as a polyatomic ion. Humans get sick from arsenate by either directly drinking the water contaminated with the ion or eating food that contains a crop that was exposed to the contaminated water during cultivation.

The arsenate issue is most prevalent in Bangladesh. At the beginning of the 1970s, Bangladesh had a cholera outbreak from surface water contamination, so UNICEF set up 10,000,000 tube wells to give Bangladeshis access to a deeper

source of groundwater. Consequently, one in five of these wells contained water laced with arsenic because arsenic from soil and industrial waste had leached into the aquifers that the tube wells pumped water from. Now, it is estimated that 57,000,000 people in Bangladesh are at risk of arsenic-induced diseases because many only have access to impure drinking water.<sup>3</sup> Countries such as India and Pakistan also experience the arsenic contamination issue. In Pakistan, most of the population's water supply comes from the Indus Plains and the Indus River. Distribution models and groundwater quality measurements performed by a Swiss Federal Institute research team indicate that there are unsafe concentrations of arsenic (greater than 10 ppb) present in the Indus River and extremely dangerous levels of arsenic (greater 200 ppb) present in the southern region of the Indus Valley. The hazard probability model calculates that roughly 50,000,000 to 60,000,000 people are reliant on the contaminated groundwater supply.<sup>4</sup>

India's first arsenic contamination case was reported in Chandigarh during 1976, and since then, cases have arisen in

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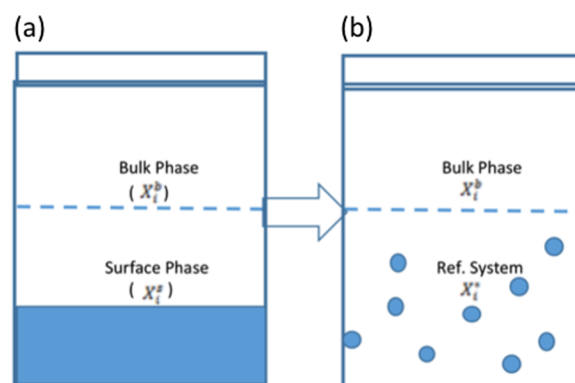
villages all throughout the country. A research survey conducted in numerous villages found that the contamination is present in seven Indian states. The percentage of people drinking the water in contaminated regions is higher than most countries because there is a high level of poverty, a lack of government oversight, and very few regulations in the isolated villages scattered throughout the country.<sup>5</sup> The arsenic problem is not only confined to Asia as there is a massive arsenic contamination issue in the west coast of the United States. For example, in California, a study conducted in the San Joaquin Valley depicted that 10% of the population in the valley was exposed to elevated levels of arsenate in their drinking water. Poor agricultural activities in the area have caused the recent elevation of arsenic since many hazardous fertilizers have leached into the groundwater.<sup>6</sup>

The objective of this research is to develop an inexpensive clay-based adsorbent with a high adsorption capacity. Since the components that make up the clay adsorbent are abundant, the cost of the newly designed adsorbent should be a fraction of the cost for the current arsenic filters. Clay-based adsorbents have been developed using computer-aided molecular design (CAMD) that are based on the adsorbate solid solution (ASS) theory.<sup>7,8</sup> In this work, a similar CAMD approach is used to generate new adsorption candidates with enhanced adsorption capabilities of arsenic. ASS theory has also been successfully used to design polymeric resin for the adsorption of copper from drinking water.<sup>9</sup> In the application of ASS theory for the design of novel adsorbents, the group contribution method (GCM) is used in the first part to estimate the interaction parameters between functional groups and adsorbate by solving for the activity coefficient. CAMD is used to find the ideal combination of the functional groups which relies on the UNIFAC interaction parameters found by GCM in the first part of this research.

## ■ BACKGROUND

**Arsenate Poisoning.** Arsenate attacks enzyme-bound thioesters, and this inhibits ATP formation during glycolysis. Therefore, it causes an impairment of respiration cells and a depletion of ATP in liver and kidney cells.<sup>10</sup> Arsenate is now classified as carcinogenic heavy metal because numerous research studies have linked arsenate to the cause of many cancers such as kidney, liver, skin, and lung.<sup>11</sup> The World Health Organization (WHO) established an international limit of 10 ppb of arsenate in drinking water for the water to be considered safe. The Environmental Protection Agency (EPA) set the same standard that the maximum contaminant level (MCL) of arsenate is 10 ppb for water to be considered safe drinking water.<sup>5</sup>

**Adsorption Process.** Adsorption is a filtration process that consists of using adhesion to separate an ion, atom, or molecule (adsorbate) from a fluid or dissolved solid and into the pores that are located on the surface of a solid (adsorbent).<sup>12</sup> Adsorption is best described in Figure 1a. Within this adsorption system, there are two preliminary phases: bulk and solid. During adsorption, the molecules from the bulk phase adhere to the surface of the solid phase until the adsorbent reaches its adsorption equilibrium.<sup>13</sup> At the adsorption equilibrium, no more adsorbate can be adsorbed since the adsorption rate and the desorption rate are equal; therefore, the adsorbent is at its maximum adsorption capacity. Adsorption equilibria are best described in an isotherm which plots the concentration of the adsorbate against the



**Figure 1.** (a) Adsorption system where total amount of fluid molecules is divided in two independent phases that are assumed to be homogeneous: the adsorbed or surface phase and the bulk phase. (b) The adsorbate solid solution is defined as the reference system,<sup>14</sup> and the bulk phase is considered to be uninfluenced by the solid.<sup>14</sup>

amount absorbed; as a result, the point where the graph begins to plateau is the maximum adsorption capacity. One of the commonly used isotherm equations is the Langmuir equation:

$$\frac{1}{q} = \frac{1}{b} + \frac{1}{(bk)C} \quad (1)$$

where  $q$  is the amount of adsorbate adsorbed in a unit mass of adsorbent, and  $C$  is the equilibrium concentration of the adsorbate inside the aqueous solution or bulk phase. There are two constants in this equation,  $b$  and  $k$ , which are determined from the adsorption data. Variables  $b$  and  $k$  specifically represent equilibrium constants. Another mathematical equation that an isotherm can graphically depict is the Freundlich equation as shown below. In this case,  $K_f$  and  $n_f$  are the Freundlich parameters.

$$q = K_f C n_f \quad (2)$$

Adsorption is a suitable technique for most separations, including ones that would have been considered impossible with distillation or ion exchange, but it is not commonly practiced, as there is currently a lack of both experimental data and suitable models that can be used to predict the equilibrium behavior of multicomponent mixtures.<sup>14,15</sup> Gathering the proper adsorption equilibrium data may be difficult as it is time consuming and cost intensive. Fortunately, the group contribution (GC) methodology utilizes the adsorbate solid solution theory which can make hundreds of adsorption estimates and calculations that would have been otherwise determined using expensive experimental measurements.

**Adsorbate Solid Solution (ASS) Theory.** The adsorbate solid solution theory (ASST) is a thermodynamic framework that describes the adsorption behavior of a fluid on a solid's surface. This theory incorporates the influence that different structural groups in the adsorbent have on the adsorption process. Excess Gibbs free energy models ( $G^E$  models) are provided by this theory, so that the activity coefficients of the adsorbed phase may be calculated. Using the activity coefficients in the surface phase and bulk phase, one may find the relationship between the phase equilibria of each adsorbed component in the surface phase (Figure 1a) and bulk phase. The relation of the phase equilibrium for each component is described below as given in Berti et al.<sup>14,15</sup>

$$x_i^b \gamma_i^b = x_i^s \gamma_i^s \exp\left(\frac{g^{\text{ad}} - g_{oi}^{\text{ad}}}{RT\Gamma_{mi}^s}\right) \quad (3)$$

where  $x_i^b$  and  $x_i^s$  are the fractions of component  $i$ .  $\gamma_i^b$  and  $\gamma_i^s$  are the activity coefficients in the bulk phase and in the surface phase, respectively.  $g^{\text{ad}}$  is the free energy of immersion in the adsorbed solution, and  $g_{oi}^{\text{ad}}$  is the free energy of immersion in the pure adsorbed species. In the denominator of eq 3,  $R$  is the ideal gas constant,  $T$  is the temperature in kelvin, and  $\Gamma_{mi}^s$  is the surface phase capacity of each adsorbent. The surface phase capacity is the ratio between the pore volume of an adsorbent ( $v_p$ ) and the molar volume of a fluid ( $v_{oi}$ ).

In the new thermodynamic framework proposed in the Berti et al.<sup>14,15</sup> literature, the adsorption system is formulated as a solution of solid and liquid adsorbates, and the adsorption system considers the influence from different structural groups in the adsorbents. Most importantly, this new framework makes the calculations of the phase equilibrium straightforward. The equation below indicates the equilibrium relation between the two phases that are in Figure 1b for component  $i$  in terms of the difference in chemical potential.

$$x_i^b \gamma_i^b = x_i^* \gamma_i^* \exp\left(\frac{\varphi^* - \varphi_{oi}^*}{RT\Gamma_{mi}^s}\right) \quad (4)$$

Here,  $x_i^*$  is the fraction of component  $i$  in the ASS phase, and  $\gamma_i^*$  is an activity coefficient.  $(\varphi^* - \varphi_{oi}^*)$  is the difference between the chemical potential of the adsorbent before undergoing adsorption and after undergoing adsorption. This chemical potential difference can be computed in terms of the excess Gibbs energy:

$$\varphi^* - \varphi_{oi}^* = \frac{1}{m_0}(G^{E*} - G^{Es} - G_{oi}^{E*}) \quad (5)$$

where  $m_0$  is the molar mass of the adsorbent,  $G^{E*}$  is the excess Gibbs free energy of the adsorbate solid solution,  $G^{Es}$  refers to the excess Gibbs free energy of the surface phase, and  $G_{oi}^{E*}$  is the excess Gibbs free energy of the component's adsorption. In equation five, all the excess Gibbs free energy variables are in joules. Excess Gibbs free energy can be expressed in terms of activity coefficients:

$$\frac{G^{E*}}{RT} = \sum_{i=0}^k n_i^* \ln \gamma_i^* \quad (6)$$

where index zero refers to the adsorbent. The activity coefficient  $\gamma_i^*$  can be solved using a modified UNIFAC model.<sup>14</sup> Similarly, the activity coefficients in the surface phase ( $x_i^s$ ) can be solved in connection to excess Gibbs free energy:

$$\frac{G^{Es}}{RT} = \sum_{i=1}^k n_i^s \ln \gamma_i^s(x_i^s) \quad (7)$$

where  $n_i^s$  is the molar quantity in the surface phase for component  $i$ , and it is computed as

$$n_i^s = x_i^s n_T^*(1 - x_0^*) \quad (8)$$

Here,  $x_i^s$  is the fraction of component  $i$  in the surface phase, and it can be calculated as

$$x_i^s = \frac{x_i^*}{(1 - x_0^*)} \quad (9)$$

For a pure component's adsorption, the activity coefficient  $\gamma_{oi}^*$  can be computed as

$$\gamma_{oi}^* = 1 + \frac{1}{\Gamma_{mi}^s M_0} \quad (10)$$

For activity coefficients of various components in the mixture can be calculated using the group contribution method described below.

**Group Contribution Method (GCM) and Modified UNIFAC Model.** In a GCM, molecules are split up into groups that are composed of individual atoms or a small group of atoms. ASST incorporates the influence of different structural groups into the GCM methodology. The parameters of the GCM are calculated as the number of times that the group shows up in the adsorbent multiplied by its contribution. The parametrized GCM could then be used to estimate binary interaction parameters between individual groups where there is no available experimental data.<sup>16</sup> This ultimately avoids the need of expensive experimentation to determine the binary interaction parameters. Additionally, this theory requires the use of the UNIFAC model similar to the model used to predict the vapor–liquid equilibrium.<sup>17</sup> A modified version of the UNIFAC model is presented by Berti et al.,<sup>15</sup> which uses the model to compute the activity coefficient in the adsorbate solid solution. The calculations for the activity coefficient  $\gamma_i^*$  is described below:

$$\ln \gamma_i^* = \ln \gamma_{oi}^* + \ln \gamma_{GE,i}^* \quad (11)$$

where  $\gamma_{GE,i}^*$  is the concentration-dependent part of the activity coefficient which is divided into a combinatorial part ( $\gamma_i^{C*}$ ) and a residual part ( $\gamma_i^{R*}$ ). The concentration dependent part of the activity coefficient ( $\gamma_{GE,i}^*$ ) is given as

$$\ln \gamma_{GE,i}^* = \ln \gamma_i^{C*} + \ln \gamma_i^{R*} \quad (12)$$

The combinatorial part is calculated by

$$\ln \gamma_i^{C*} = \ln \gamma_{GE,i}^{C*}(x_i^*) - \ln \gamma_{GE,i}^{C*}(x_{oi}^*) \quad (13)$$

and the residual part is calculated by

$$\ln \gamma_i^{R*} = \ln \gamma_{GE,i}^{R*}(x_i^*) - \ln \gamma_{GE,i}^{R*}(x_{oi}^*) \quad (14)$$

$(\gamma_{GE,i}^*)(x_{oi}^*)$  represents the activity coefficient of a pure adsorbed liquid and its adsorbent.<sup>17</sup>

**Computer-Aided Molecular Design Adsorbents.** Use of computer-aided molecular design (CAMD) for the design of novel adsorbents is typically the reverse of the group contribution method as its main objective is to develop a new molecule with desired properties which in the present case is developing a molecule with a high adsorption capacity of arsenate. Essentially, CAMD generates molecules by selecting a combination of groups which together shows desired or enhanced properties. Once the molecular equation meets the desired characteristics, the properties are estimated using a property prediction model.<sup>18</sup> CAMD has been used for the chemical product design of many different types of molecules, such as the design of a solvent with accelerated reaction kinetics,<sup>19</sup> but this is the first time that it is being used to generate an adsorbent for arsenic removal.

## METHODOLOGY

In this section, we have shown the adsorption of arsenate on three different clay-based adsorbents: zeolite, beidellite, and sepiolite. ASS theory is used to predict the binary interaction parameters between the functional groups that are found in the three adsorbents for arsenate. The experimental data comes from Bektas et al.<sup>20</sup> that report the isotherm data and the adsorption equilibrium for the three adsorbents.

**Problem Description of Arsenic Removal.** In the first part of the research, we have found the UNIFAC interaction parameters between individual groups and the adsorbate by minimizing the difference between the adsorption values generated in the model and that of the experimental values presented in Bektas et al.<sup>20</sup> The functional groups and their interaction parameters in the solid and bulk phase are identified. The water samples comprising the bulk phase came from the Eastern Black Sea regions of Turkey. In the bulk phase, the components present are water, arsenate, calcium, sodium, bicarbonate, sulfate, and silicon dioxide. The three clay-based adsorbents are zeolite, sepiolite, and beidellite. Each of the three adsorbents is divided into seven functional groups. They are silicon dioxide, sodium oxide, aluminum oxide, calcium oxide, potassium oxide, magnesium oxide, and iron (iii) oxide. The percentages of different functional groups in the three adsorbents are different.

**Mass Balance of Adsorption Process.** Three inputs had to be given for each adsorbent to run the computational model: the experimental adsorption values in moles per grams which was generated using the Langmuir isotherm, the molar fraction of all the components in the bulk phase, and the molar fraction of the adsorbent in the ASS phase. The moles of the adsorbent ( $n_0^*$ ) are calculated by

$$n_0^* = \frac{m_0}{M_0} \quad (15)$$

The moles of adsorbate ( $n_1^*$ ) in the ASS are calculated using

$$n_1^* = q^* m_0 \quad (16)$$

To find the moles of arsenic in the bulk phase at equilibrium, the moles of arsenate in the solid phase is subtracted from the initial feed of moles of arsenic in the solution as presented in eq 17

$$n_1^b = n_1^1 - n_1^* \quad (17)$$

where  $n_1^b$  is moles of arsenic in the bulk phase and  $n_1^1$  is moles of arsenate initially present in the solution. It is calculated as

$$n_1^1 = C_1 * V_{sln} \quad (18)$$

where  $C_1$  is the concentration of arsenic in moles per liter and  $V_{sln}$  is the volume of the entire solution. Based on the experiments in the Bektas et al.<sup>20</sup> paper, the volume of the solution used in our model is 100 mL, and the concentration varied between 0 and 2.5 mg/L.

The molar fraction of water, arsenate, and the five components in the bulk phase ( $x_i^b$ ) are computed using

$$x_i^b = \frac{n_i^b}{n_T^b} \quad \forall i \in [0...7] \quad (19)$$

where  $n_i^b$  is moles of that component and the  $n_T^b$  is the total moles in the bulk phase. The molar fraction ( $X_i^*$ ) can also be computed for arsenate and the adsorbent in the ASS using

$$x_i^* = \frac{n_i^*}{n_T^*} \quad \forall i \in [0 \text{ and } 1] \quad (20)$$

where  $n_i^*$  is moles of that group and the  $n_T^*$  is the total moles in the ASS. The flowchart of the adsorption process is given in Figure 2.

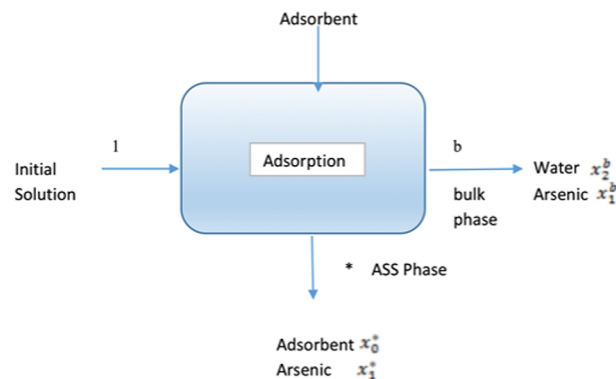


Figure 2. Flowchart of adsorption of arsenic.

**Activity Coefficient for Bulk Phase and Adsorbate Solid Solution (ASS).** The activity coefficients in the bulk phase are estimated using the UNIFAC method. The UNIFAC model is divided into two parts: the combinatorial part and the residual part as

$$\ln \gamma_i^b = \ln \gamma_i^{Cb} + \ln \gamma_i^{Rb} \quad (21)$$

where  $\gamma_i^{Cb}$  represents the activity coefficients for the combinatorial part of the bulk phase, while  $\gamma_i^{Rb}$  represents that for residual part. The combinatorial part could be calculated as

$$\ln \gamma_i^{Cb} = \ln \left( \frac{\varphi_i}{x_i^b} \right) + 5q_i \ln \left( \frac{\theta_i}{\varphi_i} \right) + l_i - \frac{\varphi_i}{x_i^b} \sum_1^j x_j^b l_j \quad (22)$$

where

$$l_i = 5(r_i - q_i) - (r_i - 1) \quad (23)$$

$$\theta_i = \frac{q_i x_i^b}{\sum_j^M q_j x_j^b} \quad (24)$$

$$\varphi_i = \frac{r_i x_i^b}{\sum_j^M r_j x_j^b} \quad (25)$$

In eq 24,  $\theta_i$  represents molecular surface area, and in eq 25,  $\varphi_i$  represents volume fraction of component i.  $q_i$  and  $r_i$  are the van der Waals surface area and van der Waal radius of component i, and they are estimated using individual functional groups van der Waals size  $R_g$  and surface area  $Q_g$  as

$$r_i = \sum_g^{N_g} \vartheta_g^{(i)} R_g \quad (26)$$

$$q_i = \sum_g^{N_g} \vartheta_g^{(i)} Q_g \quad (27)$$

Here,  $g$  progresses from 1 to  $N_{gt}$  and the total number of functional groups in the molecule.  $R_g$  and  $Q_g$  are both constants, obtained from atomic and molecular structure data. These values are given in Table 1. The residual part of the activity coefficients is calculated as

$$\ln \Gamma_g = Q_g \left[ 1 - \ln \left( \sum_1^m \theta_m \Psi_{mg} \right) - \sum_1^m \left( \frac{\theta_m \Psi_{gm}}{\sum_1^n \theta_n \Psi_{nm}} \right) \right] \quad (28)$$

Here  $m$  and  $n$  represent all the functional groups.

**Table 1. Functional Groups along with Their van der Waals Surface  $R_g$  and Volume  $Q_g$**

| Group                          | $R_g$ | $Q_g$ |
|--------------------------------|-------|-------|
| SiO <sub>2</sub>               | 1.389 | 1.267 |
| Na <sub>2</sub> O              | 1.688 | 1.407 |
| Al <sub>2</sub> O <sub>3</sub> | 1.109 | 1.109 |
| CaO                            | 1.752 | 1.438 |
| K <sub>2</sub> O               | 2.716 | 1.844 |
| MgO                            | 1.013 | 1.041 |
| Fe <sub>2</sub> O <sub>3</sub> | 1.221 | 1.167 |
| H <sub>2</sub> O               | 0.920 | 1.400 |
| Ca <sup>2+</sup>               | 1.000 | 1.000 |
| Na <sup>+</sup>                | 3.000 | 3.000 |
| HCO <sub>3</sub> <sup>-</sup>  | 0.631 | 0.737 |
| SiO <sub>2</sub>               | 1.389 | 1.267 |
| SO <sub>4</sub>                | 2.856 | 2.015 |

The group fraction ( $\chi_m$ ) and group surface area fraction ( $\theta_m$ ) is calculated as

$$x_m = \frac{\sum_j^i \vartheta_m^{(i),b} x_j}{\sum_1^j \sum_1^n \vartheta_m^{(i),b} x_j} \quad (29)$$

$$\theta_m = \frac{Q_m x_m}{\sum_1^n Q_n x_n} \quad (30)$$

The parameter  $\Psi_{nm}$  from eq 29 is given as

$$\Psi_{nm} = \exp(-a_{nm}/T) \quad (31)$$

In eq 31,  $a_{nm}$  is the group interaction parameters for the UNIFAC model; the group interaction parameter is the measure of the difference in the energy of interaction between a group  $n$  and a group  $m$  or between two of the same group  $m$ .<sup>17</sup> The energy of interaction would be the equal for two of the same groups, so the interaction parameter would equal out to be zero. Also, the interaction parameter between two groups in ASS equals zero according to Berti et al.<sup>14</sup> Tables 2 and 3

**Table 2. UNIFAC Interaction Parameters ( $aa_{nm}$ ) for ASS**

| Groups (k)                     | As(V)            | SiO <sub>2</sub> | Na <sub>2</sub> O | Al <sub>2</sub> O <sub>3</sub> | CaO              | K <sub>2</sub> O | MgO              | Fe <sub>2</sub> O <sub>3</sub> |
|--------------------------------|------------------|------------------|-------------------|--------------------------------|------------------|------------------|------------------|--------------------------------|
| As(V)                          | 0                | aa <sub>12</sub> | aa <sub>13</sub>  | aa <sub>14</sub>               | aa <sub>15</sub> | aa <sub>16</sub> | aa <sub>17</sub> | aa <sub>18</sub>               |
| SiO <sub>2</sub>               | aa <sub>21</sub> | 0                | 0                 | 0                              | 0                | 0                | 0                | 0                              |
| Na <sub>2</sub> O              | aa <sub>31</sub> | 0                | 0                 | 0                              | 0                | 0                | 0                | 0                              |
| Al <sub>2</sub> O <sub>3</sub> | aa <sub>41</sub> | 0                | 0                 | 0                              | 0                | 0                | 0                | 0                              |
| CaO                            | aa <sub>51</sub> | 0                | 0                 | 0                              | 0                | 0                | 0                | 0                              |
| K <sub>2</sub> O               | aa <sub>61</sub> | 0                | 0                 | 0                              | 0                | 0                | 0                | 0                              |
| MgO                            | aa <sub>71</sub> | 0                | 0                 | 0                              | 0                | 0                | 0                | 0                              |
| Fe <sub>2</sub> O <sub>3</sub> | aa <sub>81</sub> | 0                | 0                 | 0                              | 0                | 0                | 0                | 0                              |

show the interaction parameters in the ASS and bulk phase, respectively. Some of the interactions are found in the literature, and the unknowns are solved using the UNIFAC model as given in these series of equations.

## ■ OPTIMIZATION PROBLEM

**Optimization of Interaction Parameters.** The first objective of this research is to calculate the UNIFAC interaction parameters (i.e.,  $aa_{nm}$  and  $ab_{nm}$ ) that are not found in the literature by using optimization techniques. The parameter estimation problem involves solving a series of equations that are presented in the Methodology section using empirical data found in the literature. An error function (Err) serves as the objective function, and it equals the square root of the difference between the adsorption capacity of the experimental values ( $q^{exp}$ ) and the adsorption capacity of the calculated values ( $q^{cal}$ ) which are obtained from the thermodynamic model. The closeness of  $q^{exp}$  and  $q^{cal}$  indicates how accurate the interaction parameters were since the interaction parameters acted as the decision variable in the model.

The sum of the errors between the  $q^{cal}$  and  $q^{exp}$  values was minimized using a nonlinear programming (NLP) optimization solution method. Specifically, we used the nonlinear least-square fit for this purpose. Thirty experimental points are converted into individual objective functions, and then the error function for the entire adsorbent adds up each of the individual objective functions at each experimental point and squares the total at the end. Each objective function takes the square root of the difference between the  $q^{cal}$  value and the  $q^{exp}$  value (one of the 30 experimental points). This regression optimization method is expressed as

$$\min \text{Err} = \min \sum_1^{AD} \sum_1^{Eq} [q_{Eq,AD}^{cal} - q_{Eq,AD}^{exp}]^2 \quad (32)$$

where AD indicates which adsorbent was used, and the variable Eq is the total number of equations used to solve the problem, which typically revolved around 20 for all the three adsorbents. The adsorption capacity that the UNIFAC model calculates can be represented as

$$q^{cal} = \frac{x_i^* n_T^*}{m_0} \quad (33)$$

where,  $x_i^*$  can be found in eq 20 which signifies the fraction of component  $i$  in the ASS phase, and  $n_T^*$  is the total moles in the ASS that is calculated as

$$n_T^* = \frac{(\phi^* - \phi_{oi}^*) m_0}{RT \left( (x_0^* \ln \gamma_0^* + x_1^* \ln \gamma_1^*) - x_{01}^* \ln \left( 1 + \frac{1}{\Gamma_{mr}^* M_0} \right) \right)} \quad (34)$$

Additionally, the excess Gibbs free energy of the adsorbate–solid solution ( $G^{E*}$ ), excess Gibbs free energy of the surface phase ( $G^{Es}$ ), and the excess Gibbs free energy of the pure component adsorption ( $G^{E*_{oi}}$ ) are given in terms of the activity coefficient below, respectively:

$$\begin{aligned} G^{E*} &= RT(n_0^* \ln \gamma_0^* + n_1^* \ln \gamma_1^*) \\ &= RT(x_0^* n^* \ln \gamma_0^* + x_1^* n^* \ln \gamma_1^*) \end{aligned} \quad (35)$$

Table 3. UNIFAC Interaction Parameters ( $ab_{nm}$ ) for Bulk Phase<sup>a</sup>

| Groups (k)       | As(V)            | H <sub>2</sub> O | Ca               | Na               | HCO <sub>3</sub> | SO <sub>4</sub>  | SiO <sub>2</sub> |
|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| As(V)            | 0                | ab <sub>12</sub> | ab <sub>13</sub> | ab <sub>14</sub> | ab <sub>15</sub> | ab <sub>16</sub> | ab <sub>17</sub> |
| H <sub>2</sub> O | ab <sub>21</sub> | 0                | -897.2           | 22.38            | -982.5           | ab <sub>26</sub> | 17869.84         |
| Ca               | ab <sub>31</sub> | -838.2           | 0                | NA               | 4166.3           | ab <sub>36</sub> | ab <sub>37</sub> |
| Na <sup>+</sup>  | ab <sub>41</sub> | -165             | NA               | 0                | 6342.2           | ab <sub>46</sub> | ab <sub>47</sub> |
| HCO <sub>3</sub> | ab <sub>51</sub> | ab <sub>52</sub> | ab <sub>53</sub> | ab <sub>54</sub> | 0                | ab <sub>56</sub> | ab <sub>57</sub> |
| SO <sub>4</sub>  | ab <sub>61</sub> | -185624.64       | ab <sub>63</sub> | ab <sub>64</sub> | ab <sub>65</sub> | 0                | ab <sub>67</sub> |
| SiO <sub>2</sub> | ab <sub>71</sub> | -1156.9          | ab <sub>73</sub> | ab <sub>73</sub> | ab <sub>75</sub> | ab <sub>76</sub> | 0                |

<sup>a</sup>The known values of  $a_{nm}$  can be found in Kikic et al.<sup>21</sup>

Table 4. ASS UNIFAC Interaction Parameters ( $aa_{nm}$ ) Calculated

| Groups                         | As(V)   | SiO <sub>2</sub> | Na <sub>2</sub> O | Al <sub>2</sub> O <sub>3</sub> | CaO     | K <sub>2</sub> O | MgO     | Fe <sub>2</sub> O <sub>3</sub> | Na+    |
|--------------------------------|---------|------------------|-------------------|--------------------------------|---------|------------------|---------|--------------------------------|--------|
| As(V)                          | 0       | -150080          | 1222.1            | 1768.2                         | -1487.9 | 84.969           | -3134.5 | 6171.8                         | 6857.1 |
| SiO <sub>2</sub>               | 1811.6  | 0                | 0                 | 0                              | 0       | 0                | 0       | 0                              | 0      |
| Na <sub>2</sub> O              | 4059.9  | 0                | 0                 | 0                              | 0       | 0                | 0       | 0                              | 0      |
| Al <sub>2</sub> O <sub>3</sub> | 2015.1  | 0                | 0                 | 0                              | 0       | 0                | 0       | 0                              | 0      |
| CaO                            | 10096   | 0                | 0                 | 0                              | 0       | 0                | 0       | 0                              | 0      |
| K <sub>2</sub> O               | 2098.8  | 0                | 0                 | 0                              | 0       | 0                | 0       | 0                              | 0      |
| MgO                            | 823.043 | 0                | 0                 | 0                              | 0       | 0                | 0       | 0                              | 0      |
| Fe <sub>2</sub> O <sub>3</sub> | -11950  | 0                | 0                 | 0                              | 0       | 0                | 0       | 0                              | 0      |
| Na <sub>2</sub> O              | 1080.3  | 0                | 0                 | 0                              | 0       | 0                | 0       | 0                              | 0      |

$$G^{Es} = RT(n_1^s \ln \gamma_1(x_1^s)) = RT(n^s x_1^s \ln \gamma_1(x_1^s)) \quad (36)$$

$$G_{0i}^{E*} = RTn_{0i}^* \ln \gamma_{0i}^* = RTx_{0i}^* n^* \ln \left( 1 + \frac{1}{\Gamma_{mi}^s M_0} \right) \quad (37)$$

Here,  $\chi_{0i}^*$  equals  $\chi_1^*$  since arsenic is the only adsorbate. To compute  $\phi^* - \phi_{0i}^*$  in terms of activity coefficients rather than excess Gibbs free energy, the equation below is used

$$\phi^* - \phi_{0i}^* = -RT\Gamma_{mi}^s \ln \left( \frac{x_i^b \gamma_i^b}{x_i^* \gamma_i^*} \right) \quad (38)$$

**Optimization for CAMD of Adsorbents To Remove Arsenate.** The primary objective for the second part of this research is to create a new adsorbent with a high adsorption capacity so that the adsorbent can be cost efficient. The new adsorbent is going to be composed of seven functional groups that come from the three adsorbents, and the CAMD will determine which combination of the groups produces the highest adsorption capacity. Adsorption capacity ( $q$ ) is defined as the amount of adsorbate that an adsorbent can take up per unit mass; therefore, higher the adsorption capacity, fewer of the adsorbent is needed. Since arsenic is a large-scale problem around the world, decreasing the amount of adsorbent needed could save numerous developing countries and areas affected by arsenic contamination a massive amount of money. The goal of maximizing the new objective function is presented as

$$\max q = \frac{(n_1^1 - n_1^b)}{m_0} \quad (39)$$

Here, molar mass of the adsorbent ( $m_0$ ) and initial moles of arsenate in the solution ( $n_1^1$ ) are two constants. Fewer the moles of arsenic in the bulk phase ( $n_1^b$ ) more the adsorption is since moles of arsenate in the bulk phase is being negated from the constant  $n_1^1$ . A large value for the objective function is a positive thing as it indicates that a relatively large amount of arsenate has been adsorbed from the bulk phase.

The objective function presented in eq 39 is subject to a set of linear and nonlinear equality and inequality constraints. These constraints range from structural feasibilities, boundaries for the decision variable, and thermodynamic equilibrium restrictions. The problem is given restrictions such that it must pass the standards mandated in the TCLP (toxicity characteristic leaching protocol), which is set by the Environmental Protection Agency (EPA). The TCLP determines if a hazardous waste meets the definition of EPA Toxicity.

Each iteration involves starting with a given number of initial moles of the solution ( $n_1^1$ ), then estimating the number of moles of arsenate in the bulk phase, and last selecting a combination of functional groups with its thermodynamic equilibrium meeting the equilibrium constraints and staying within the tolerance. The thermodynamic equilibrium constraint is represented as

$$\left| x_i^b \gamma_i^b - x_i^* \gamma_i^* \exp \left( \frac{(\phi^* - \phi_{0i}^*)}{RT\Gamma_{mi}^s} \right) \right| \leq tol \quad (40)$$

The structural feasibility constraint is represented as

$$\sum_{g=1}^{N_{gt}} Val(K_g)^* K_g = 0 \quad (41)$$

where  $K_g$  is the decision variable, which specifies the number of times that each group occurs inside the molecule of the newly design adsorbent. The index  $g$  designates the functional group being evaluated, which would be between one and eight. The groups are SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O, MgO, K<sub>2</sub>O, CaO, Fe<sub>2</sub>O<sub>3</sub>, and Na<sup>+</sup>.  $K_g$  is constrained to be an integer between 1 and 20, val ( $K_g$ ) is the valence of each group, and  $N_{gt}$  is the total groups used to form the molecule. Essentially, the CAMD creates a molecule that is composed of a combination of functional groups with the desire properties, and this molecule is constrained to meet certain conditions. Both the interaction parameter generation and the CAMD are performed with a novel metaheuristic optimization algorithm called efficient ant

Table 5. Bulk Phase UNIFAC Interaction Parameters ( $ab_{nm}$ ) Calculated

| Groups           | As(V)    | H <sub>2</sub> O | Ca     | Na     | HCO <sub>3</sub> | SO <sub>4</sub> | SiO <sub>2</sub> |
|------------------|----------|------------------|--------|--------|------------------|-----------------|------------------|
| As(V)            | 0        | -7914.1          | 2073.3 | 6857.1 | 2715.1           | -1897           | 19262            |
| H <sub>2</sub> O | 758.381  | 0                | -897.2 | 22.38  | -982.5           | 461.16          | 17870            |
| Ca               | 2878.9   | -838.2           | 0      | NA     | 4166.3           | -1367.4         | 2700.5           |
| Na <sup>+</sup>  | 1080.3   | -165             | NA     | 0      | 6342.2           | 4507.1          | 1482.1           |
| HCO <sub>3</sub> | 2086.8   | -24755           | 1963.3 | 10798  | 0                | -8330.4         | -846.11          |
| SO <sub>4</sub>  | 2636.4   | -185624.64       | 6779.8 | -6699  | 377.66           | 0               | 7574.6           |
| SiO <sub>2</sub> | 376.7528 | -1156.9          | 2294.7 | -10017 | 2920.5           | -7800.8         | 0                |

colony optimization (EACO) developed in-house by Gebressie and Diwekar.<sup>22</sup>

## RESULTS AND DISCUSSION

In the first part of this research, 44 UNIFAC interaction parameters are determined using the group contribution method. After the model runs, the modified UNIFAC model found the optimal set of interaction parameters. Tables 4 and 5 contain the calculated interaction parameters between all the functional groups in the adsorbents and all the components in the bulk phase. It seems that the interaction between arsenic ions and silicon dioxide are very high. The error objective function for sepiolite is  $1.1622 \times 10^{-9}$ , beidellite is  $2.4096 \times 10^{-9}$ , and zeolite is  $3.6830 \times 10^{-9}$ . This conclusively means that the  $q^{cal}$  and  $q^{exp}$  values are very close. Figure 3a, b, and c depict the isotherms for the three adsorbents'  $q^{cal}$  and  $q^{exp}$  values validating this conclusion.

In the second part of this research, the ideal combination of functional groups is determined using a computer-aided molecular-design (CAMD) where the interaction parameters from the first part of the research along with a list of constraints are used to select optimum adsorbent using the EACO algorithm. Countless possible combinations of functional groups were considered to find the optimal clay-based adsorbent with the highest adsorption capacity. At the end, 10 candidates of adsorbents were selected with the highest adsorption capacity out of the possible  $21^8$  combinations. Table 6 lists the 10 best candidates found by the EACO algorithm. Table 6 includes the combination of functional groups that yield the highest adsorption, the mass of the new adsorbent, percent of arsenic adsorbent, and the mass of arsenic adsorbed. Most importantly, Table 6 indicates that the 10 new adsorbents have an adsorption capacity of 99.999% on average for both low and high concentrations of arsenate in drinking water. These theoretical results are extremely promising, but further experimentation is required for validation.

In Table 6, the most prevalent groups that show up in the newly formed adsorbents are sodium oxide, iron (iii) oxide, and calcium oxide. The candidates with the highest adsorption capacity tend to have these three groups be most abundant in the molecule. Significantly, these groups commonly show up in the standard adsorbents for arsenic removal. In fact, the AdEdge DWS-2S filter is an arsenic filter with a high removal capacity using its iron oxide-based media. Unfortunately, most filters like this are not economical for developing countries; therefore, it is significant that this research involved designing a clay-based adsorbent with extremely abundant groups as it creates a solution that is sustainable. The current adsorbents in the field are not as sustainable as the novel adsorbents created according to the computation model used in this paper.

The leading adsorbents in the field include granular titanium dioxide and iron-modified activated carbon. These two

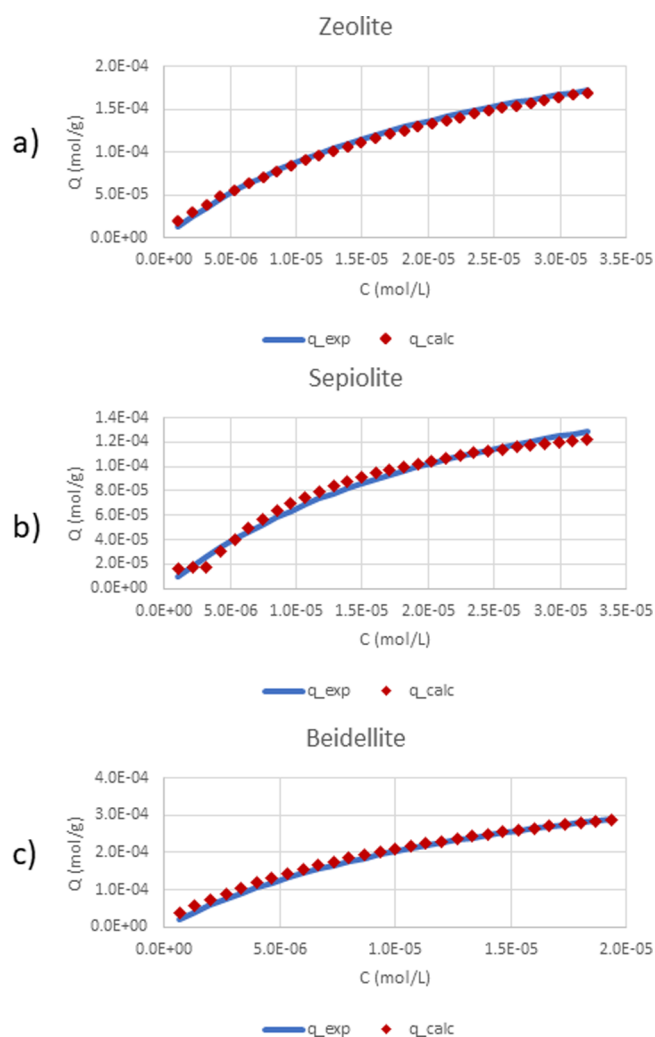


Figure 3. Comparison of the experimental adsorption capacity found in literature and the calculated adsorption capacity. (a) Isotherm for adsorption of arsenic using zeolite. (b) Isotherm for adsorption of arsenic using sepiolite. (c) Isotherm for adsorption of arsenic using beidellite.

adsorbents have been categorized as the adsorbents with the highest removal capacity in the comparative evaluation that Nicomel et al. conducted.<sup>23</sup> The adsorption capacity of granular titanium dioxide is 41.4 mg/g, and the adsorption capacity of Iron-modified activated carbon is 51.3 mg/g, while the adsorption capacity of the proposed novel adsorbents is roughly an order of magnitude higher than these adsorbents. The adsorption capacity of the adsorbent ranked one in Table 6 is 589.5 mg/g,

Table 6. Adsorption Capacity of 10 Novel Adsorbents

| Ranks | Amount adsorbed (mol/g) | Grams of new adsorbent | % Adsorbed | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | Na <sub>2</sub> O | MgO | Fe <sub>2</sub> O <sub>3</sub> | K <sub>2</sub> O | CaO |
|-------|-------------------------|------------------------|------------|------------------|--------------------------------|-------------------|-----|--------------------------------|------------------|-----|
| 1     | 0.0078678               | 0.0084823              | 99.999     | 0                | 15                             | 17                | 0   | 20                             | 0                | 15  |
| 2     | 0.0066062               | 0.010102               | 99.999     | 8                | 0                              | 20                | 0   | 20                             | 0                | 13  |
| 3     | 0.0035754               | 0.018666               | 99.999     | 10               | 10                             | 20                | 0   | 12                             | 0                | 13  |
| 4     | 0.0027271               | 0.024472               | 99.999     | 0                | 9                              | 11                | 15  | 18                             | 10               | 14  |
| 5     | 0.002443                | 0.027318               | 100        | 3                | 10                             | 17                | 12  | 20                             | 0                | 10  |
| 6     | 0.00094963              | 0.070277               | 99.999     | 12               | 8                              | 20                | 0   | 9                              | 4                | 13  |
| 7     | 0.00061781              | 0.10802                | 100        | 5                | 19                             | 20                | 13  | 12                             | 16               | 13  |
| 8     | 0.00035464              | 0.18818                | 100        | 5                | 7                              | 14                | 17  | 9                              | 2                | 17  |
| 9     | 0.00012584              | 0.53035                | 100        | 6                | 13                             | 9                 | 20  | 13                             | 12               | 12  |
| 10    | 0.00010343              | 0.64524                | 99.999     | 5                | 0                              | 6                 | 0   | 0                              | 0                | 20  |

## CONCLUSIONS AND FUTURE WORK

This paper derived interaction parameters for groups responsible for arsenic removal from existing adsorbents. The CAMD approach was used to design new adsorbents with an enhanced adsorption capacity. There was a significant change between the adsorption capacity of the currently available three adsorbents and the newly design ones; the adsorption capacity increased by more than 1 order of magnitude. This essentially means that the new adsorbent can theoretically remove roughly 10 times more arsenic than beidellite, zeolite, and sepiolite. The substantial increase in Na<sub>2</sub>O, Fe<sub>2</sub>O<sub>3</sub>, and CaO groups in the new adsorbent contributed the most toward creating a highly successful adsorbent. Only four groups out of the possible seven are present in the adsorbent candidate with the highest adsorption capacity: Na<sub>2</sub>O, Fe<sub>2</sub>O<sub>3</sub>, CaO, and Al<sub>2</sub>O<sub>3</sub>. According to CAMD, a combination of these four groups met the constraints established in the [Optimization for CAMD of Adsorbents To Remove Arsenate](#) section and still possesses the optimal adsorption capacity. It can be concluded that the adsorbate solid solution theory has been successfully applied for the design of novel clay-based adsorbents for the removal of arsenate in drinking water.

There are numerous ways to expand on this research. For example, this research methodology and models could be applied toward other heavy metals that pollute and contaminate drinking water around the world. The optimization algorithms used in this research could be reapplied toward finding a novel adsorbent for arsenite, another organic form of arsenic. Arsenite is another major form of arsenic that is present in water; therefore, future research in arsenite remediation would help in the fight toward ending arsenic contamination in drinking water.

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### Notes

The authors declare no competing financial interest.

## NOMENCLATURE

Ag = van der Waals surface area (cm<sup>2</sup>/mol)  
 $a_{nm}$  = interaction parameters  
 b = Langmuir constant  
 C = equilibrium concentration in solution (mol/L)  
 C<sub>1</sub> = initial concentration of arsenic in solution (mol/L)  
 Eq = total number of equation used to solve the problem

G<sup>E</sup> = Gibbs excess free energy (J)

$g^{ad}$  = free energy of immersion of the adsorbed solution (J/kg)

$h_1$ ;  $h_2$  = height of sphere segments (Å)

K = Langmuir constant

$k_f$  = Freundlich constant

l = bond distances (Å)

$m_0$  = mass of adsorbent (g)

M<sub>0</sub> = molecular weight of adsorbent (g/mol)

MW = molecular weight (g/mol)

$m_a$  = auxiliary parameter

N<sub>gt</sub> = total functional groups

N<sub>A</sub> = Avogadro number

$n_f$  = Freundlich constant

J = Jacobian

n = molar quantity (moles)

q = amount adsorbed for unit mass of adsorbent (mol/g)

$q_i$  = parameter for VanderWaal surface calculation

Q<sub>g</sub> = van der Waals group surfaces of group K (m<sup>2</sup>)

$r_i$  = parameter for van der Waal volume calculation

$r_w$  = van der Waals radius (Å)

$r_1$ ;  $r_2$  = van der Waals radii for both atoms (Å)

R<sub>g</sub> = van der Waals group volumes of group K (m<sup>3</sup>)

R = ideal gas constant (8.314 J/mol K)

T = temperature of adsorption (K)

$v_p$  = pore volume of the adsorbent (cm<sup>3</sup>/g)

$v_{oi}$  = molar volume of the respective fluid (cm<sup>3</sup>/mol)

Vg = van der Waals volume (cm<sup>3</sup>/mol)

V = volume (L)

x = molar fraction

%A = percentage of adsorption

## Greek Letters

$\gamma$  = activity coefficient

$\gamma_{GE,i}^*$  = activity coefficient of a binary adsorbate solid solution

$\varphi^*$  = chemical potential of the wetted solid adsorption of the pure component i (J/g)

$\varphi_{oi}^*$  = chemical potential of the wetted solid adsorption of the pure component i (J/g)

$\varphi_i$  = volume fraction for UNIFAC calculation

$\theta_i$  = surface area fraction for UNIFAC calculation

$\Gamma_{mi}^s$  = surface phase capacity of component i (mol/g)

$\rho$  = density (g/mL)

## Subscripts

i = component i

0 = adsorbent

1 = adsorbate (arsenic)

2, 3, 4 = component 2, 3, or 4

0<sub>i</sub> = pure component i or pure adsorbed component i

g = group index



j = number of components  
 T = total  
 Sln = solution  
 H<sub>2</sub>O = water

### Superscripts

E\* = excess adsorbate solid solution  
 Es = excess of the surface phase  
 l = initial feed  
 \* = adsorbate solid solution  
 b = bulk phase  
 n = adsorbate solid solution  
 s = surface phase  
 ad = adsorption  
 C = combinatorial  
 R = residual in ASS  
 Cb = combinatorial in bulk phase  
 Rb = residual in the bulk phase  
 C\* = combinatorial in ASS phase  
 R\* = residual in the ASS phase  
 cal = calculated  
 exp = experimental  
 opt = optimal  
 s = surface phase

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