

Coupling a Feedforward Network (FN) Model to Real Adsorbed Solution Theory (RAST) to Improve Prediction of Bisolute Adsorption on Resins

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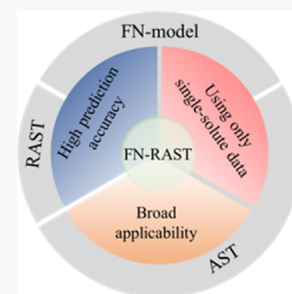


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ABSTRACT: When predicting bisolute adsorption, the adsorbed solution theory (AST) and real adsorbed solution theory (RAST) either frequently show high prediction deviations or require bisolute adsorption data. Emerging feedforward network (FN) models can provide high prediction accuracy but lack broad applicability. To avoid those limitations, adsorption experiments were performed for a total of 12 single solutes and 55 bisolutes onto two widely used resins (MN200 and XAD-4). Different FN-based models were then built and compared with AST and RAST, based on which a new modeling strategy coupling FN to RAST and requiring only single-solute data was proposed. The root-mean-square error (RMSE) of predictions by the FN-RAST is 0.082 log units for 50 bisolute adsorption on MN200, much lower than that by AST (0.164) and slightly higher than that by RAST (0.069) or the best FN model (0.068). The FN-RAST model further provided satisfactory predictions for 5 bisolute adsorption on XAD-4 (RMSE = 0.10), which is comparable to that by RAST (0.10) and much lower than those by AST (0.26) and FN model (0.38). Therefore, the FN-RAST enjoys both satisfactory prediction accuracy and some broad applicability. The values of Abraham descriptors E and S were also founded to help assess/compare the nonideal behavior in different bisolute mixtures.



INTRODUCTION

Predictive models are crucial for research and application of adsorption in water treatment. Although predictive models for single-solute adsorption have been extensively reported,^{1–5} bi- or multisolute adsorption represents a much more realistic scenario, but their predictive models are much less investigated.⁶ In the natural environment or water treatment processes, there are almost always multiple organic pollutants coexisting;^{7–9} they allow competitive and/or synergistic adsorption among the cosolutes to make their adsorption behaviors much more complex than in single-solute adsorption.^{10–12} Because of difficulty in quantifying the complex adsorption behaviors, the prediction of the adsorption capacity of bi- and multisolute mixtures suffers great uncertainties. Building accurate predictive models for bi- and multisolute adsorption is thus important for addressing these uncertainties.

Various classical and emerging predictive models have been developed for bisolute adsorption,^{13–15} among which the adsorbed solution theory (AST), a thermodynamically consistent model with a concrete theoretical foundation (details in Text S2, Supporting Information),¹⁶ has been the most successful and widely used. The most attractive feature of AST is that it can predict the adsorption of bisolute mixtures relying solely on single-solute adsorption data, which has allowed it to be used in thousands of studies to predict the adsorption of bisolute mixtures.¹⁷ Generally, AST achieves good predictions for binary gaseous/aqueous adsorption when

the adsorbates behave ideally. An ideal behavior here means that each of the solutes in the adsorbed phase behaves independently under the control of spreading pressure with the presence of the other solutes. In other words, there are no considerable interactions between the molecules of the bisolutes in the adsorbed phase.¹⁸ However, AST has shown very high deviations when bisolute mixtures behave nonideally, i.e., deviate from the ideal behavior.^{16,18} For example, AST achieves accurate predictions for the bisolute adsorption of toluene/ethylbenzene on an adsorption column¹⁹ and acetone/propionitrile on a granular activated carbon (GAC),²⁰ but it has shown high prediction deviations on the bisolute adsorption of *p*-chlorophenol/*p*-cresol, trichloroethylene/tetrachloroethylene, and phenol/*m*-cresol on GAC^{20–22} and phenanthrene/pyrene on natural sediments.²³ These prediction deviations or the nonideal behaviors of the solutes are largely associated with the lateral interactions among the different adsorbed solutes.²⁴ The more significant the lateral interactions, the higher the nonideality and then the prediction deviation by AST.^{25–28}

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To reduce high deviation in AST predictions, the activity coefficient (γ_i) as the correcting factor to account for the nonideality has been introduced to AST to form the real adsorbed solution theory (RAST).^{6,29} The γ_i can be calculated from bisolute experimental data (details in Text S2, Supporting Information) and then correlated with the fractions of the solutes in the adsorbed phase by models such as the Wilson equation and nonrandom two-liquid model (NRTL).^{24,30} The obtained correlations can then be used by RAST to predict bisolute adsorption. However, RAST requires bisolute adsorption data to calculate γ_i , which means that RAST cannot predict bisolute adsorption only based on single-solute adsorption data like AST does.^{31,32} The fitting models for γ_i also need experimental data of bisolute adsorption such as the adsorbed amounts.^{6,29} These limitations have greatly restricted the applicability of RAST. So, RAST is often employed in retrospective modeling rather than predictive modeling.²⁵

Other than the classical AST and RAST, feedforward networks (FNs) have emerged as a useful tool to build predictive models for single- or bisolute adsorption.^{33–35} FN models typically use the properties of solutes/adsorbents as the input and adsorbed amounts or adsorption coefficients as the output. An FN model can be quickly built with suitable inputs/outputs and then provide predictions for new inputs. So far, single-solute adsorption modeling has taken advantage of this easy-to-build feature of FN models to yield satisfactory prediction results.^{36,37} Several studies have also employed FN to build accurate predictive models for binary or ternary adsorption.^{34,35,38} For example, one study on gaseous binary adsorption uses the binary equilibrium concentrations together with the corresponding single-solute adsorbed amounts as the inputs and the corresponding bisolute adsorbed amounts as the outputs.³⁴ In another research, similar inputs are used for building an FN model to predict aqueous bisolute adsorption.³⁵ A recent study compares the performance of AST and FN models in predicting the adsorption of ternary nitrobenzene, phenol, and aniline on GAC.³⁸ The inputs and outputs are the three equilibrium concentrations and three adsorbed amounts of the ternary system, and the trained FN model provides excellent predictions. Despite the good prediction accuracy, one major limitation of the existing bisolute FN models cannot be overlooked; that is, they are generally a simple extrapolation of the single-solute FN models by doubling the inputs/outputs on one or several bisolute mixtures, so they lack the broad applicability provided by AST and are only applicable to certain bisolute mixtures or adsorbents that have been involved in the modeling process.

The adsorbed amount of any chemical mainly depends on three sets of parameters including properties of the chemical, equilibrium concentration, and properties of the adsorbent. Solution properties such as pH would also affect adsorption, but for the adsorption of neutral chemicals on nonionic resins, effects of solution properties are not expected to be significant. The adsorption of different bisolute mixtures under the same equilibrium concentration can be very different even on one adsorbent; similarly, the adsorption of one bisolute mixture onto different adsorbents would significantly differ even under the same equilibrium concentration. So, to accurately predict the adsorbed amounts of various bisolute mixtures on different adsorbents under changing equilibrium concentrations, all those three sets of parameters need to be incorporated in the predictive model. However, the existing bisolute FN models only include one or two sets of those parameters, so they are

only applicable to the bisolute mixtures or adsorbent(s) that have been included. For example, one bisolute FN model that solely uses equilibrium concentrations as the input without considering the properties of the chemicals/adsorbents fails to identify differences among various bisolute mixtures.³⁸ It means that this type of FN model can only predict the adsorption of the same bisolute mixtures on the employed adsorbent. Similarly, another type of FN model using bisolute equilibrium concentrations plus two single-solute adsorbed amounts as the input also suffers from some limitation.³⁵ It can predict the adsorption of different bisolute mixtures, but the predictions are limited to the employed adsorbent. The reason is that the properties of the chemicals have been incorporated implicitly by including the single-solute adsorbed amounts, which depend on the properties of the chemicals and can help quantify the differences in the lateral interactions between various bisolute mixtures;³⁵ however, this type of FN model fails to incorporate the properties of the adsorbents. As a result, the applicability of the existing FN models is restricted to one or several bisolute mixtures on one adsorbent, and the extrapolation to new bisolute mixtures or other adsorbents would inevitably lead to high deviations. Unfortunately, it is not practical to directly include properties of adsorbents in bisolute FN models because, unlike single-solute FN models, bisolute FN models require much more data. For example, for the adsorption of 10 chemicals on 10 adsorbents, single-solute adsorption needs a maximum of 100 isotherms, while bisolute adsorption needs 450 bisolute isotherms. It is challenging to conduct so many experiments when dealing with multiple chemicals and adsorbents, and there are also limited experimental bisolute adsorption data reported.

Because AST, RAST, and FN models all have their own limitations, using any of them alone cannot fulfill the goal of building broadly applicable predictive models for the adsorption of different bisolute mixtures onto different adsorbents within a wide range of solute concentrations. In this work, we for the first time established a coupled modeling strategy that can take advantage of both the broad applicability of AST and the high accuracy of FN models. To this end, comprehensive adsorption experiments for both single- and bisolute adsorption were conducted on two widely examined polystyrene-based polymeric resins MN200 (microporous) and XAD-4 (macroporous). AST predictions were first made based on the single-solute adsorption data and compared with the experimental bisolute adsorption data for each resin. Four FN models using different inputs were then built for MN200 and the prediction accuracies were compared with that of AST. The limitation of the obtained FN models was discussed by comparing their prediction for bisolute adsorption on XAD-4 with that on MN200. Note that the FN models here were built based on the bisolute adsorption data on MN200. The bisolute adsorption data for both MN200 and XAD-4 were then modeled with RAST after obtaining activity coefficients based on the bisolute experimental data, and the model performance was compared with that of the best FN model. Finally, a coupled modeling strategy named FN-RAST (see the flowchart in Figure S1), which only required single-solute adsorption data, was developed and validated based on the bisolute data on MN200, the broad applicability of the FN-RAST was validated by evaluating its prediction performance on the bisolute adsorption on XAD-4, and a qualitative relationship was obtained based on the FN-RAST model for assessing the degree of nonideality of different bisolute mixtures.

Table 1. Input Compositions of Different FN-Based Models

Model	Equilibrium Concentration		Adsorbed Amount		Abraham Descriptors	
	C_1	C_2	q_{s1}	q_{s2}	Solute 1	Solute 2
FN-model 0	✓	✓				
FN-model 1, FN-RAST 1	✓	✓	✓	✓		
FN-model 2, FN-RAST 2	✓	✓			✓	✓
FN-model 3, FN-RAST 3	✓	✓	✓	✓	✓	✓

MATERIALS AND METHODS

Chemicals and Resins. Chemicals used in this research included phenol (Acros Organics, 99%), mequinol (Acros Organics, 99%), *p*-chlorophenol (Acros Organics, 99+%), *p*-methylphenol (Acros Organics, 99+%), *m*-nitrophenol (Alfa Aesar, 98+%), aniline (Acros Organics, 99.8%), *p*-methylaniline (Acros Organics, 99%), *p*-chloroaniline (Alfa Aesar, 98%), *p*-nitroaniline (Acros Organics, 99%), vanillin (Sigma-Aldrich, 99%), and caffeine (Sigma-Aldrich, 99%). All chemicals were used as received without further purification. MN200 was provided by Purelite and had a BET surface area and a total pore volume of 1021 m²/g and 0.49 cm³/g separately. XAD-4 was purchased from Sigma-Aldrich and had a BET and a total pore volume of 829 m²/g and 1.25 cm³/g separately.⁴ More detailed information about the selection of chemicals and resins can be found in Text S1 and Table S1. Before usage, the resins were subjected to extensive washing with 0.1 M HCl, 0.1 M NaOH, and DI water to remove inorganic impurities. Then, Soxhlet extraction with methanol was used to remove organic impurities. The purified resins were air-dried and used for all the experiments.

Adsorption Experiments. Of the 12 selected chemicals, 9 chemicals (aniline, *m*-nitrophenol, nitrobenzene, *p*-chloroaniline, *p*-chlorophenol, *p*-cresol, phenol, *p*-nitroaniline, and *p*-toluidine) have been extensively examined in wastewater treatment research, 2 chemicals (caffeine and mequinol) are used as pharmaceutical and personal care products, and 1 additive (vanillin) exists in some industrial eluents and is related to color generating.³⁹ All single- and bisolute adsorption experiments were conducted in 20, 40, or 60 mL glass bottles with PTFE-lined caps; each sample was prepared in triplicates. After adding a suitable amount of resin (typically 10–15 mg of MN200 or 25–30 mg of XAD-4) and stock solutions of target chemicals, the bottles were shaken on a 180 rpm shaker at 23 °C for 48 h for the adsorption to reach equilibrium. In every bisolute adsorption experiment, the fraction of the solutes in the adsorbed phase was carefully controlled to vary between around 10 and 90% (more in Text S1). The reason for such an arrangement is that the activity coefficients are highly related to the fractions of solutes in the adsorbed phase, a wide range of which can maximize the application scope of the obtained models.

The concentrations of the solutes in the supernatants were measured by an HPLC (Agilent 1260) coupled with a DAD detector and Agilent Eclipse XDB-C18 column (4.6 × 250 mm; 5 μm; mobile phase, methanol:water: 67:33 with a flow rate of 1 mL/min) at the beginning and end of the adsorption experiments. Then, the adsorbed amounts of each solute were calculated by mass balance according to the measured initial and equilibrium concentrations. There were a total of 50 groups of bisolute adsorption experiments performed on

MN200 for the model development and another 5 on XAD-4 to validate the developed modeling strategy.

MODEL DEVELOPMENT

AST and RAST Predictions. The single isotherms were fitted with different adsorption isotherm models, including Langmuir, Freundlich, and the quadratic equation used in our previous research.⁴⁰ The best-fitting model was selected as the working isotherm, and the best-fitting parameters were then used to calculate the adsorbed amounts in bisolute adsorption. The AST equations (Text S2 and eqs S5–S9) were solved in Matlab 2019a (details of the code and input data setup are given in Texts S2 and S3). The inputs were 6 fitting parameters for 2 single-solute isotherms (m_1 , n_1 , k_1 , m_2 , n_2 , and k_2) and 2 equilibrium concentrations (C_1 and C_2) in the bisolute adsorption system; the outputs are 2 bisolute adsorbed amounts (q_1 and q_2).

The workflow for RAST includes the following three steps: (1) the single-solute adsorption isotherms together with the bisolute adsorption equilibrium concentrations were employed to calculate q_i using eqs S5–S9, (2) the experimental activity coefficients for each solute were calculated by eqs S6 and S14, and (3) the calculated activity coefficients were used to perform RAST predictions by eqs S5–S9 (more details in Text S2).

Polyparameter Linear Free Energy Relationships (pp-LFERs). Polyparameter linear free energy relationships (pp-LFERs) use Abraham descriptors (E , S , A , B , and V)⁴¹ to build regression equations (eq 1) and have been widely used to predict different specific partitions (SPs). One of the most common applications is to build single-solute predictive models for aqueous adsorption,^{42–44} in which multilinear regression (MLR) is performed between the adsorption coefficient $\log K_d$ and the Abraham descriptors. With the obtained MLR equations, adsorption coefficients of new chemicals (with known Abraham descriptors) can be calculated.^{2,45} Our recent work has also demonstrated that FN with the Abraham descriptors can build powerful predictive models for single-solute adsorption on carbon materials and resins.³⁶

$$SP = e \cdot E + s \cdot S + a \cdot A + b \cdot B + v \cdot V + c \quad (1)$$

where e , s , a , b , v , and c are the fitting parameters and SP is the specific partition such as $\log K_d$ of the chemicals under the equilibrium concentration C_e . The Abraham descriptors E , S , A , B , and V capture nonspecific interactions arising from induced dipoles, stable polarity (i.e., dipole–dipole interactions), H-bonding accepting and donating, and cavitation energy and part of London dispersive forces beyond what is captured by the E term, respectively.

In our previous research,⁴⁰ pp-LFERs helped build MLR models for the activity coefficients in bisolute adsorption under

Table 2. Fitting Parameters for the Single-Solute Adsorption Isotherms ($\ln q_i = m_i \cdot (\ln C_i)^2 + n_i \cdot \ln C_i + k_i$) on MN 200 and the Abraham Descriptors of the Target Chemicals

chemical	abbreviation	quadratic equation				Abraham descriptors				
		m	n	k	R^2	E	S	A	B	V
aniline	ANI	−0.0347	0.981	1.7477	1	0.96	0.96	0.26	0.41	0.8162
caffeine	Caff	−0.0313	0.704	3.396	0.998	1.5	1.82	0.08	1.25	1.36
mequinol	MOP	−0.0229	0.685	3.5531	0.999	0.9	1.17	0.57	0.48	0.9747
<i>m</i> -nitrophenol	NP	−0.0512	1.013	2.766	0.997	1.05	1.57	0.79	0.23	0.9493
nitrobenzene	NB	−0.0414	0.897	3.796	0.999	0.87	1.11	0	0.28	0.8906
<i>p</i> -chloroaniline	CA	−0.0471	0.964	3.194	0.997	1.06	1.13	0.3	0.31	0.939
<i>p</i> -chlorophenol	CP	−0.0366	0.789	3.633	0.994	0.92	1.08	0.67	0.2	0.898
<i>p</i> -cresol	MP	−0.0309	0.752	3.489	0.999	0.82	0.87	0.57	0.31	0.916
phenol	PHE	−0.0404	1.055	1.456	1	0.81	0.89	0.6	0.3	0.7751
<i>p</i> -nitroaniline	NA	−0.0492	1.005	3.029	0.998	1.22	1.91	0.42	0.38	0.991
<i>p</i> -toluidine	MA	−0.0328	0.798	3.493	0.997	0.92	0.95	0.23	0.45	0.9571
vanillin	Van	−0.0184	0.61	4.243	1	1.03	1.28	0.33	0.68	1.1313

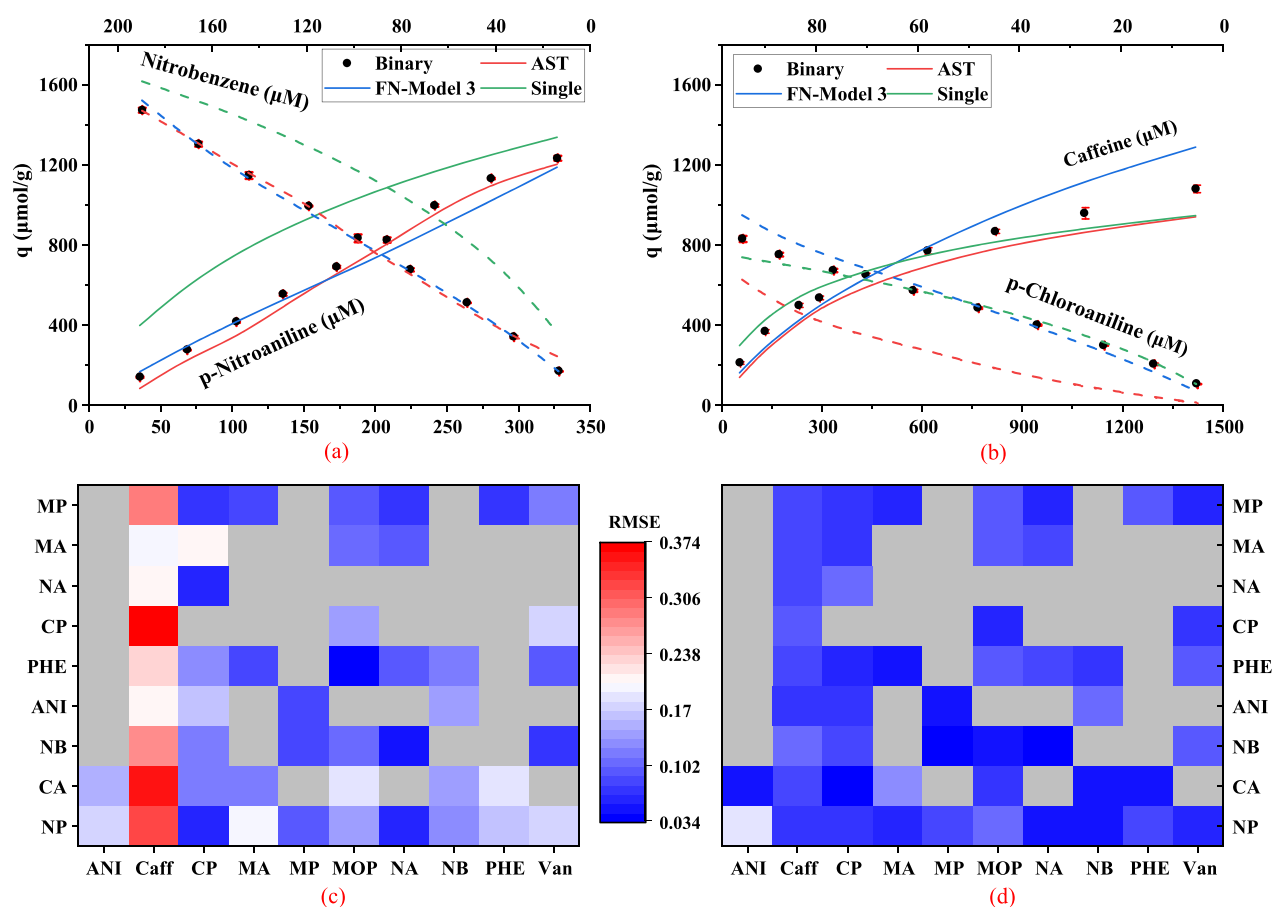


Figure 1. Single- and bisolute adsorption isotherms on MN200 for mixtures of (a) *p*-nitroaniline (solid lines) and nitrobenzene (dashed lines) and (b) caffeine (solid lines) and *p*-chloroaniline (dashed lines) based on either the experimental data (symbols) or model fits (lines), (c) RMSE heat map for the AST model, and (d) RMSE heat map for FN-model 3. For any bisolute mixtures, each bisolute isotherm included 9 equilibrium concentrations. Each square in (c) and (d) represents the adsorption of a bisolute mixture, and the color changes from blue to red indicate increased RMSEs in the predictions. Note that the gray color indicates missing values.

infinite dilute conditions and provided predictions for several bisolute mixtures. The results indicated that pp-LFERs are helpful in capturing interactions between different adsorbed solutes. However, the predictions are limited to the selected bisolute mixtures on one type of resin. In this research, pp-LFERs were included in FN-based models to account for interactions between the adsorbed solutes in bisolute adsorption.

FN Models. Four FN models were built with different inputs but all used the bisolute adsorbed amounts (q_1 and q_2) as the output (Table 1). FN-model 0 only used two equilibrium concentrations (C_1 and C_2) as the input. FN-model 1 used C_1 , C_2 , and two single-solute adsorbed amounts (q_{s1} and q_{s2} , corresponding to the adsorbed amount of each solute under C_1 and C_2 but in single-solute adsorption) as the input. These two models have been used in the published

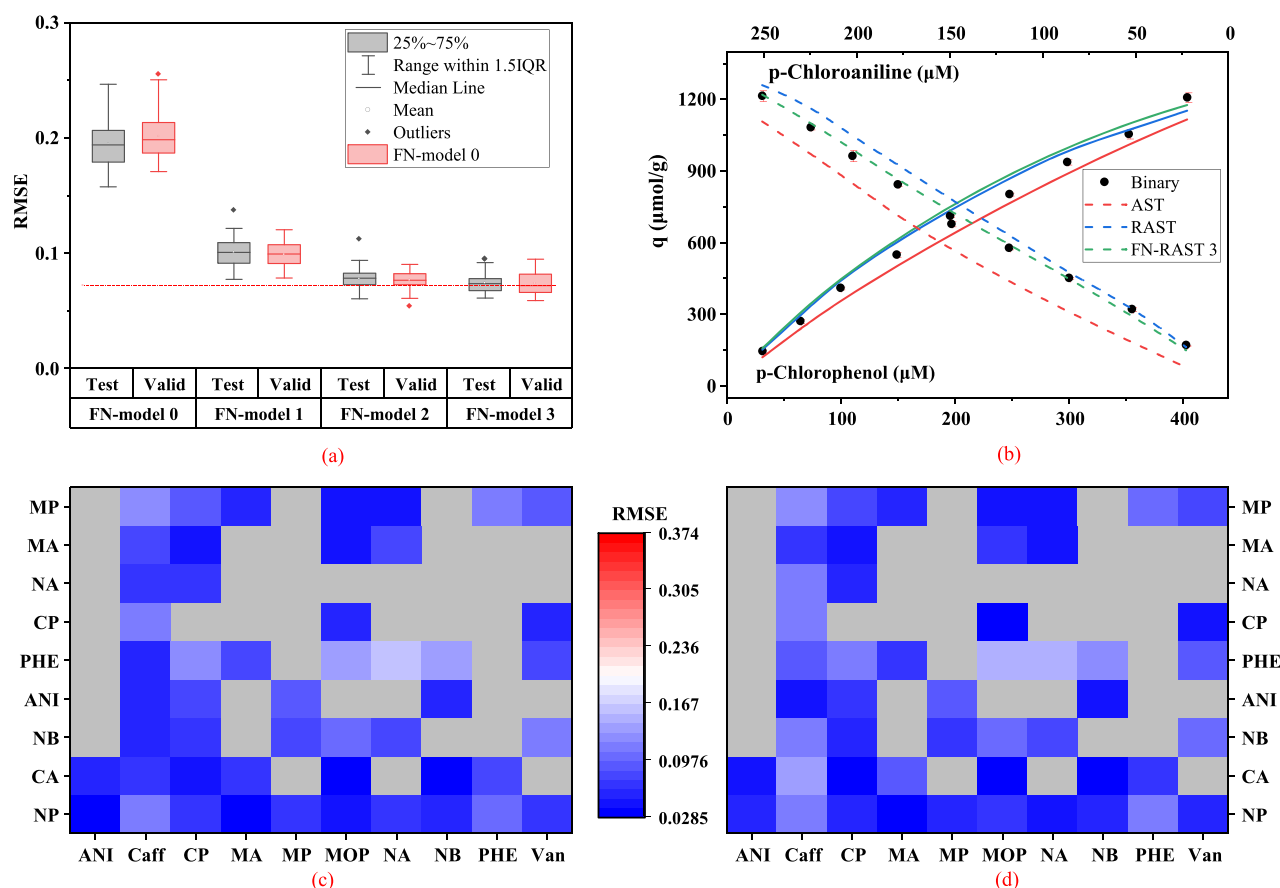


Figure 2. (a) Comparison among the four FN models for bisolute adsorption on MN200, (b) bisolute adsorption isotherms of *p*-chlorophenol (solid lines) and *p*-chloroaniline (dashed lines) based on either the experimental data (symbols) or different model fits (lines), (c) RMSE heat map for the RAST model, and (d) RMSE heat map for the FN-RAST 3. Note that the gray color indicates missing values.

studies^{34,35,38} and hence were employed for comparison. Following the strategy in our single-solute predictive models where the Abraham descriptors were used in the input,³⁶ two additional models were built by extending single-solute FN models to bisolute FN models. FN-model 2 added Abraham descriptors for both solutes to the inputs. For FN-model 3, q_{s1} and q_{s2} were further added.

FN-RAST Models. The FN-RAST can be divided into two consecutive modules including the FN module and RAST module. The FN module is used to predict activity coefficients, and the RAST module uses the obtained activity coefficients to solve the RAST equations for bisolute adsorbed amounts. Combining the two modules, three FN-RAST models (Table 1) were built based on the data of bisolute adsorption on MN200, and the final outputs were still q_1 and q_2 . Similar to the FN models, FN-RAST 1 used C_1 , C_2 , q_{s1} , and q_{s2} as the input, FN-RAST 2 used Abraham descriptors, C_1 , and C_2 as the input, and FN-RAST-3 further included q_{s1} and q_{s2} based on FN-RAST 2 (Table 1). The best FN-RAST model was tested on MN200 first and then on XAD-4. Note that the three FN-RAST models only differ in the FN module and the RAST module is identical except using different activity coefficient values from the FN module.

We employed two training strategies to build the FN models and FN-RAST models: one is to randomly split the whole dataset into the training, validation, and test sets by a ratio of 0.6:0.2:0.2, and the other is the leave-one-out cross-validation, where the “one” means entire paired bisolute isotherms

(referred as one “group” hereafter). The first strategy was to tune the hyperparameters for the FN-based models, and the second was to evaluate the prediction performance of the FN or FN-RAST models (more details in Text S4).

Evaluation Metric. The root-mean-square error (RMSE) was used to quantify the deviations of different model predictions from the experimental values. The equation to calculate RMSE is shown in eq 2, where x_{pred} and x_{exp} represent the predicted and experimental values of x , respectively.

$$\text{RMSE} = \sqrt{\frac{\sum_{i=1}^n (x_{\text{pred}} - x_{\text{exp}})^2}{n}} \quad (2)$$

RESULTS AND DISCUSSION

Single-Solute Adsorption Isotherms. For single-solute adsorption on MN200 and XAD-4, three adsorption isotherm models including Langmuir, Freundlich, and a quadratic equation were used to fit the adsorption data (more discussion in Text S1). The quadratic equation (Table 2) gave the best fitting with all the R^2 values higher than 0.99. The Freundlich model could fit the adsorption isotherms within the low-equilibrium-concentration regions, but the fitting curves significantly deviated from the experimental data in the high-concentration regions. The Langmuir model can only fit some of the adsorption isotherms. So, only the fitting results by the quadratic equation are shown here (Table 2 and Table S2). Given the best fitting by the quadratic equation for all the

single isotherms, it was chosen as the fitting isotherm for AST-related calculations (more details in Text S2).

Bisolute Adsorption Isotherms on MN200. Different bisolute mixtures showed different adsorption patterns. As the bisolute mixture of *p*-nitroaniline/nitrobenzene (Figure 1a) taken as a typical example, both *p*-nitroaniline and nitrobenzene showed significantly lower adsorbed amounts (black circles) in the bisolute adsorption than in the respective single-solute adsorption (green lines). The lower adsorbed amounts suggest that some competitions happened in the bisolute adsorption. Similar competitions in adsorption have also been reported in other bisolute adsorption studies.^{11,12} However, the results for the bisolute adsorption when caffeine was involved were different (an example in Figure 1b). In the low-equilibrium-concentration region for caffeine, which was the high-concentration region for the other solute (such as *p*-chloroaniline), the adsorption of caffeine was slightly suppressed compared to that in the single-solute system, but in the high-concentration region for caffeine where the other solute was in its low-concentration region, there was a substantial increase in the caffeine adsorption. Such phenomena suggest that strong interactions may exist between caffeine and other solutes to promote the adsorption of caffeine, similar to what was believed to be synergistic effects in bisolute adsorption of phenol/aniline on resin.¹⁰ Note that the impact of caffeine on the *p*-chloroaniline adsorption was not much affected. The adsorption data for all single- and bisolute mixtures are shown in Tables S4 and S5.

AST and FN Model Predictions for Bisolute Adsorption on MN200. AST generally works well on many bisolute mixtures but has high prediction deviations in some cases especially when caffeine was one of the solutes (Figure 1a–c). The lateral interactions between caffeine and the other solute in the bisolute mixtures may be the reason for the nonideality (more discussion later). The RMSE by AST for the adsorption of 50 bisolute mixtures on MN200 varied between 0.035 and 0.37 log units with an overall RMSE of 0.164 log unit. For the binary adsorption involving caffeine, the RMSE of AST varied between 0.20 and 0.37 log units (Figure 1c).

Unlike AST, the four FN models showed significantly different prediction accuracies (Figure 2a), indicating that the input compositions have considerable influences on the performance of the models. FN-model 0 achieved a good prediction in the reported ternary adsorption research³⁸ but provided very poor prediction in this research. In the work that used FN to build a ternary adsorption model,³⁸ there is only one ternary-solute mixture and the training and validation datasets both have the same three chemicals; therefore, no additional parameters are needed for the ternary-solute mixture. In this research, diverse and distinctly different sets of bisolute mixtures were allocated to the training and validation datasets. Different bisolute mixtures can have significantly different adsorption patterns even under the same equilibrium concentration. FN-model 0 that uses equilibrium concentrations as the only input treats different bisolute mixtures equally, which is a clear oversimplification. Although it has been proved to be straightforward and powerful in the reported ternary adsorption prediction, it can only be used to predict ternary adsorption that shares the same chemicals with the training set. Therefore, the applicability of FN-model 0 is very limited and its poor prediction in this work is expected.

To improve the prediction accuracy of FN-model 0, the single-solute adsorbed amounts q_{s1} and q_{s2} that serve as the descriptors for distinguishing between different bisolute mixtures were added to build FN-model 1, and the results indicate that the prediction accuracy was significantly improved (Figure 2a). q_{s1} and q_{s2} may help differentiate the adsorption behavior of each chemical in bisolute adsorption systems because different chemicals generally have different adsorbed amounts under a certain equilibrium concentration. Similarly, the two solutes in binary mixtures would generally have different q_{s1} and q_{s2} ; thus, they can also help describe differences between various bisolute mixtures. So, this model can provide well-improved prediction for different bisolute mixtures. However, q_{s1} and q_{s2} may fail to capture all the lateral interactions between different adsorbed solutes in bisolute adsorption; thus, there are still considerable deviations in the predictions by FN-model 1.

Following the strategy used in the single-solute predictive models,³⁶ FN-model 2 was built by incorporating the Abraham descriptors of both solutes in the bisolute mixtures as part of the input. The results show that FN-model 2 can satisfyingly predict the adsorbed amounts of each solute (Figure 2a), suggesting that the powerful prediction capability of the descriptors is also capable of relating to adsorption of bisolute mixtures. The Abraham descriptors here may distinguish between various bisolute mixtures as well as capture at least part of the interactions between the adsorbed solutes.

Inspired by the above improvement in FN-model 2, q_{s1} and q_{s2} were further introduced to build FN-model 3. The addition of q_{s1} and q_{s2} also improved the prediction compared with FN-model 2. This is because q_{s1} and q_{s2} together with the Abraham descriptors may help capture more information about the interactions among the adsorbed solutes, which in turn provides further improvements. Overall, the predictions by FN-model 3 for the 50 bisolute adsorption achieved RMSEs between 0.021 and 0.12 log units with an overall RMSE of 0.068, and the predictions were significantly improved compared with that by AST (Figure 1d).

Despite the success in the FN models, AST rather than FN models is widely accepted and has become a benchmark method for bi- or multicomponent adsorption prediction. This is because AST can be used to predict either gas-phase or aqueous-phase bisolute adsorption on different adsorbents relying solely on single-solute adsorption isotherms. The prediction accuracy of AST is also generally acceptable, although it shows high prediction deviations in many cases. In contrast, existing FN models or the newly developed FN models in this research are only applicable to one or several bisolute adsorption on one adsorbent even though their prediction accuracy is high, and the extrapolation of FN models to other adsorbents is largely unreliable and may be very poor.

RAST and FN-RAST. To improve the prediction accuracy by AST, we tested RAST that incorporates activity coefficients on all the bisolute mixtures on MN200. The results suggest that RAST achieved considerable improvements compared with AST (Figure 2c), especially for the adsorption of bisolute mixtures involving caffeine, and the prediction deviations were slightly higher than those by FN-model 3. The RMSEs of the predictions by RAST varied between 0.01 and 0.15 with an overall RMSE of 0.069 log units.

However, RAST itself has a substantial limitation in the predictive modeling because it requires bisolute adsorbed

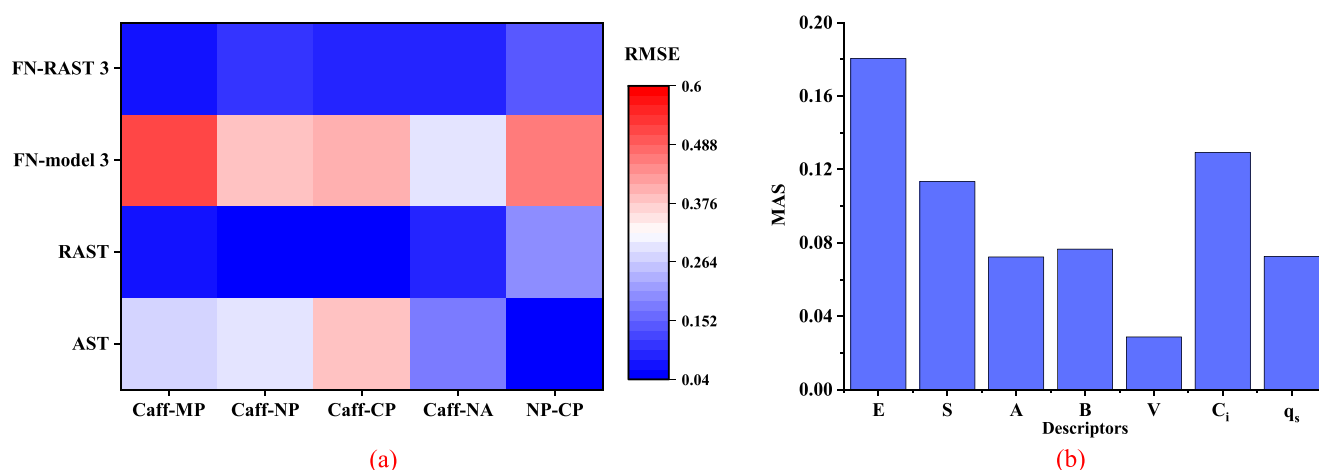


Figure 3. (a) RMSEs of different models in predicting the bisolute adsorption on XAD-4. The x-axis indicates different bisolute mixtures, and y-axis indicates different models. The color of each rectangular indicates the RMSE of the prediction for a bisolute mixture by one of the models. The overall RMSEs for the adsorption of the five bisolute mixtures on XAD-4 are 0.51, 0.10, 0.10, and 0.28 log units for FN-model 3, FN-RAST 3, RAST, and AST, respectively. (b) Mean absolute Shapley values for different input descriptors concerning the nonideality.

amounts to calculate the experimental activity coefficients, which means that it is impossible to predict the adsorption of other bisolute mixtures that do not have experimental bisolute adsorption data. The activity coefficients determined for a bisolute mixture onto one adsorbent also cannot be directly applied to the same bisolute mixture on another adsorbent.

So far, we have demonstrated that AST, RAST, and FN models have their own merits, but each method alone has substantial difficulties in building predictive models for bisolute adsorption that have both broad applicability and low prediction deviations. Therefore, we would like to couple these modeling approaches into the so-called FN-RAST strategy to take advantage of their merits while avoiding the limitations. In this new strategy, the FN module is first used to predict activity coefficients based on only single-solute adsorption data. The predicted activity coefficients are then employed as the input into RAST to predict bisolute adsorbed amounts. The underlying rationale for this strategy is that the nonideality as reflected by the activity coefficients can be largely attributed to the interactions among the adsorbed solutes on an adsorbent,^{26,28} and the activity coefficient of one solute in the adsorbed phase is highly related to its fraction in the adsorbed phase.^{24,30} The existing FN models have been able to accurately predict bisolute adsorption;^{32,33} thus, it is a reasonable extrapolation that FN models can also predict the fractions of solutes in the adsorbed phase and then activity coefficients with considerable accuracy. If this is the case, then well-improved predictions can be achieved by the FN-RAST strategy. Moreover, the FN module for predicting activity coefficients mostly focuses on capturing interactions among the adsorbed solutes without being specific to certain adsorbents. The obtained model based on some bisolute mixtures can be applied to the adsorption of not only the same but also new bisolute mixtures onto new adsorbents. So, the predictive models using the FN-RAST strategy can achieve a balance between accuracy and broad applicability.

Similar to the FN models, three FN-RAST models with different input compositions (Table 1) were obtained. Not surprisingly, FN-RAST 3 with the Abraham descriptors, C_1 , C_2 , q_{s1} , and q_{s2} as the input provided the best predictions (Figure 2d and Figure S4), which showed considerable improvements compared with those by AST and were comparable or only

slightly inferior to the predictions by the RAST. The RMSEs of the predictions by FN-RAST 3 varied between 0.03 and 0.15 log units with an overall RMSE of 0.082 log units. Understandably, FN-RAST 3 did not perform better than RAST because RAST relied on the experimentally determined activity coefficients, whereas FN-RAST relied on the modeled activity coefficients. Nevertheless, the FN-model predicted activity coefficients can address a large portion of the nonideality derived from interactions among the adsorbed solutes in bisolute mixtures.

Validation of the FN-RAST 3 on XAD-4. To test the applicability of the built models to other adsorbents, another five bisolute adsorption experiments were conducted on XAD-4, and the bisolute adsorption data were employed to evaluate the prediction performance of the built models (Figure 3a and Figure S5). The AST, FN-model 3, and FN-RAST 3 require only single-solute adsorption data on XAD-4 as the input data, while the RAST requires both single- and bisolute adsorption data on XAD-4 to make predictions. The AST predictions for XAD-4 followed a similar pattern as those on MN200, with high deviations obtained for the bisolute mixtures involving caffeine. The similarity in the prediction deviations confirmed that the nonideality in the bisolute adsorption is largely due to interactions among the adsorbed solutes (more discussion below). Similarly, the predictions were significantly improved by RAST. For FN-model 3 that was built based on the bisolute adsorption data on MN200, its predictions for the bisolute adsorption on XAD-4 have very high deviations, although its predictions on MN200 have little deviations (Figure 1b). Such a drastic difference in the prediction accuracy reveals the limitation of the FN models as they only capture the bisolute adsorption information specific to one adsorbent and cannot be applied to other adsorbents.

To solve the limitation of FN-model 3, a series of bisolute adsorption experiments need to be performed on various adsorbents and a new FN model with the properties of different adsorbents in the input has to be built. However, compared with single-solute adsorption experiments, bisolute adsorption experiments are much more time-consuming and labor-intensive. Therefore, it is not realistic to build predictive models for bisolute adsorption on each adsorbent.

Because the nonideality is largely derived from the interactions among different adsorbed solutes, the FN-RAST strategy is promising in capturing the dominant interactions to achieve good predictions, as indicated by its prediction for the bisolute adsorption on MN200. So, FN-RAST 3 was further tested on XAD-4 to validate its broad applicability. The FN-RAST 3 was used to obtain the activity coefficients and then bisolute adsorbed amounts on XAD-4 with single-solute adsorption isotherms, C_1 , and C_2 . Note that only the bisolute adsorption data for MN200 were used to build the FN-RAST 3. The results for FN-RAST 3 (Figure 3a) showed that the predictions were significantly improved (RMSE = 0.10) compared with those by FN-model 3 (RMSE = 0.51) or AST (RMSE = 0.28) and were also comparable with those by RAST (RMSE = 0.10). This means that the FN-RAST 3 can provide not only low deviations like RAST but also a broad predictive ability like AST. It only needs single-solute adsorption information but is applicable to various bisolute mixtures on different adsorbents.

Qualitatively Determining the Nonideality and Limitation of FN-RAST. Nonideal behavior has been observed in the above bisolute mixtures as well as in other gaseous/aqueous multicomponent adsorption; however, the degree of the nonideality varies significantly among different bisolute mixtures. As shown in the bisolute adsorption on MN200, AST can well predict the majority of the bisolute mixtures with high deviations only for several mixtures. It means that not all bisolute adsorption requires further correction for the AST predictions. Therefore, it is beneficial to know the relative extent of the nonideality in different bisolute mixtures and whether the activity coefficients are necessary for correction.

Unfortunately, relationships or methods to determine the nonideality or to compare it among different bisolute mixtures are unavailable for aqueous bisolute adsorption, which makes the nonideality in bisolute mixtures hard to track even qualitatively, not to mention quantitatively. To better understand sources of the nonideality concerning the input descriptors in bisolute mixtures, the mean absolute Shapley (MAS) value based on Shapley theory was examined.^{46,47} The Shapley theory has been developed to fairly distribute the “payout” among the descriptors based on the coalitional game theory,⁴⁸ where the payout refers to the nonideality calculated as $(1 - \gamma_i)$. This is especially suitable for quantifying the contributions of all descriptors that are not equal, which is the case here for the three sets of descriptors.⁴⁶ A more positive or negative Shapley value means that the descriptor has a larger positive or negative contribution to nonideality and vice versa. The Shapley values were first calculated for each descriptor at every experimental data point and the MAS was then calculated using the Shapley values (details in Text S5).^{47,49,50} The results (Figure 3b) indicate that E , S , B , and A have significant contributions to the nonideality, and the V shows the least influence. Within a bisolute mixture, C_i and q_s also show considerable influences over the nonideality, which is understandable because a high C_i or q_s would inevitably lead to a high possibility for interactions among the adsorbed solutes and, hence, high nonideality. This finding agrees with the results from previous research that molecular interactions among the adsorbed solutes are the dominant contributor to the nonideality.³⁵ Taking the bisolute mixtures involving caffeine as an example, caffeine has relatively high E , S , and B values (Table 2), and those bisolute mixtures indeed showed

higher nonideality than those without caffeine. Similarly, for the reported bisolute adsorption of toluene/ethylbenzene or acetone/propionitrile,^{19,20} they all have relatively low values for E , S , and B (Table S3). This means that the lateral interactions among the adsorbed solutes are not very strong and the nonideality is negligible. Indeed, AST achieved satisfying predictions for both of the bisolute mixtures. On the contrary, p -chlorophenol/ p -cresol, trichloroethylene/tetrachloroethylene, phenanthrene/pyrene, and phenol/ m -cresol generally have higher E , S , and B values, which suggests that stronger lateral interactions possibly exist among the adsorbed solutes. Thus, nonideality cannot be neglected and high prediction deviations by AST are expected and indeed observed.^{20–23} With this simple rule that the E , S , and B terms of chemicals play key roles in the nonideality in bisolute adsorption (either in or outside the experimental range), we can now make a qualitative assessment of the accuracy of AST-based predictions for different bisolute mixtures, and this assessment can help determine whether a further correction of AST is needed.

Limitations of FN-Based Models. The FN algorithm provides an attractive solution for adsorption prediction because one can easily build predictive models by feeding a certain amount of data to the FN. However, limitations associated with FN cannot be neglected. One major limitation is that the applicability of FN models highly relies on the available source data. For example, FN-model 3 that was built only using adsorption data on MN200 achieved good prediction for bisolute adsorption on MN200 but poor prediction for that on XAD-4. It can be expected that FN-model 3 would not provide good predictions for other nonionic resins. For comparison, AST can be reasonably applied to bisolute adsorption on different resins and other adsorbents, even though the prediction accuracy is not always satisfactory. For FN-model 3, a series of bisolute adsorption experiments on XAD-4 and/or other nonionic resins will be needed to achieve satisfactory predictions for these resins. As stated in Introduction, batch bisolute adsorption experiments are labor-intensive, and it is impossible to perform bisolute adsorption on every nonionic resin. Also, this problem is not unique in adsorption prediction because other experimental fields may also face this problem as far as FN-based predictive models are concerned. Therefore, FN is not a universal substitute for classical modeling methods, and it always remains an important question about how to balance the prediction accuracy and applicability when using the FN algorithm.

Although the newly developed modeling strategy has achieved a good balance between the prediction accuracy and broad applicability, FN-RAST 3 and the qualitative assessment for nonideality also suffer from limitations that are inherent to activity coefficients. The activity coefficient is not a perfect method for nonideality correction. It mostly accounts for lateral interactions among the adsorbed solutes but overlooks possible nonideality caused by heterogeneity of the adsorbent surfaces.⁵¹ So, there are still prediction deviations. A more comprehensive method that can incorporate both interactions between the adsorbed solutes and heterogeneity of the adsorbent surfaces would help predict bisolute adsorption better. Similarly, the qualitative relationship only considers the interactions among the adsorbed solutes. A quantitative relationship would lead to a better

determination of the nonideality and understanding of the origin of nonideality in bisolute adsorption.

Environmental Significance. The classical AST and RAST models have shown incompetence in dealing with complex adsorption scenarios, but it does not mean that they are totally obsolete; the emerging FN models have received some momentum but cannot cope with all the complexities and their limitations cannot be overlooked. This research demonstrates a promising path for future model development, that is, to couple the emerging FN-based models to the classical RAST. As shown in the results, the prediction accuracy by FN-RAST 3 for the adsorption of 50 bisolute mixtures on MN200 is comparable to the prediction accuracy by RAST, but FN-RAST 3 only uses single-solute experimental data, whereas RAST requires bisolute adsorption data. More importantly, FN-RAST 3 can be easily applied to the adsorption of bisolute mixtures on another resin (XAD-4) while still based on single-solute adsorption data. Compared with the existing models, the new strategy greatly extends the prediction ability to the adsorption of various bisolute mixtures onto different adsorbents and achieves a balance between the prediction accuracy and applicability. Also, the proposed models in this research can handle some more complex scenarios such as adsorption in unknown backgrounds (Text S6) after suitable modification(s). It is now possible to build broad predictive models for bisolute adsorption on various adsorbents relying on adsorption data onto only several types of adsorbents. The burden of batch experiments will be greatly reduced, while the applicability remains almost unchanged. In addition, a comprehensive set of bisolute adsorption data covering 55 different bisolute mixtures onto two resins were experimentally obtained. Such a database not only assisted the model development in current research but also will help future model development with data from other studies using this coupled modeling strategy.

Through the MAS method, factors that influence the nonideality are semiquantified to explain the differences in the AST prediction accuracy for different bisolute mixtures. This finding can help qualitatively compare the degree of nonideality among different bisolute mixtures and determine whether additional corrections are needed when using AST in the bisolute adsorption prediction. Our recent research has built promising predictive models for single-solute adoption.³⁶ The current research moves another key step forward toward adsorption prediction of more realistic solute mixtures. In summary, the new modeling strategy together with the comprehensive bisolute experimental data will make a major contribution to future research on the predictive modeling of bi- and multisolute adsorption.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.est.0c03700>.

More detailed explanation of methods in this study, the figures and tables mentioned in the main text, and additional figures and tables to support the training process (PDF)

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Notes

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