

Separation Science and Engineering

Adsorption of 2-naphthalenesulfonic acid/sulfuric acid/sulfurous acid from aqueous solution by iron-impregnated weakly basic resin: Equilibrium and model☆

Changhai Li^{1,2,*}, Dongmei Jia^{1,2}¹ Department of Chemical Engineering, Binzhou University, Binzhou 256603, China² Research Center of Chemical Engineering and Technology, Binzhou University, Binzhou 256603, China

ARTICLE INFO

Article history:

Received 31 January 2016

Received in revised form 22 March 2016

Accepted 23 March 2016

Available online 7 April 2016

Keywords:

2-naphthalenesulfonic acid

Hybrid iron impregnated D301

Adsorption

Non-ideal competitive adsorbed model

Model

Equilibrium

ABSTRACT

Commercial grade weakly basic resin D301 was impregnated with iron through a simple method using ferric chloride. Experiments for single, bisolute and trinary competitive adsorption were carried out to investigate the adsorption behavior of 2-naphthalenesulfonic acid (NSA), sulfuric acid and sulfurous acid from their solution at 298K onto the novel hybrid iron impregnated D301(Fe-D301). Adsorption affinity of NSA on Fe-D301 was found to be much higher than that of sulfuric acid, while adsorption affinity of sulfuric acid was slightly higher than that of sulfurous acid. The data of single-solute adsorption were fitted to the Langmuir model and the Freundlich adsorption model. The non-ideal competitive adsorbed model coupled with the single-solute adsorption models were used to predict the bisolute and trinary-solute competitive adsorption equilibria. The NICM coupled with the Langmuir model yields the favorable representation of the bisolute and trinary-solute competitive adsorption behavior.

© 2016 The Chemical Industry and Engineering Society of China, and Chemical Industry Press. All rights reserved.

1. Introduction

Effluent from dye manufacturing that contains 2-naphthalenesulfonic acid (NSA) can cause serious pollution and affect water quality when it is discharged into the environment. The removal of NSA from wastewater can be carried out by ion exchange, solvent extraction, reverse osmosis, chemical oxidation and adsorption. Adsorption holds promise in the treatment of wastewater, as it is inexpensive, simply designed, easy to handle, and provides sludge-free cleaning operation [1,2]. Many adsorbents have been investigated for wastewater treatment, including activated carbon, sludge ash, cashew nut shells, and polymers [2–6]. Weakly basic resin ion exchange resin is used to remove contaminants in water treatment processes because of its huge specific surface area and well-developed pore structures [7,8]. Review of literature shows that adsorption capacity of adsorbent increased significantly by surface modification [9–12]. Surface modification involves functionalization of the adsorbent surface with new groups that may provide new sites for adsorption of solutes from aqueous solutions. Iron hydroxides have high adsorption capacities, large surface areas, and the capability to adsorb both anions and cations. Therefore, impregnating iron hydroxide

nanoparticles on the macroporous polystyrene anion exchanger (D301) may improve the capacity of the resins.

In present study, a simple method was to use ferric salt solution as the precursor and precipitate ferric onto commercial weakly basic D301resin. Fe-D301 was used as an adsorbent for the removal of NSA, H₂SO₄ and H₂SO₃ from their aqueous solutions. It had good selectivity, large capacity and is easy for regeneration.

2. Materials and Methods

2.1. Materials

All reagents used were of AR grade and obtained from Shanghai Chemical Reagent Station (Shanghai, China). Stock solutions of NSA, sulfuric acid and sulfurous acid were prepared with double distilled water. The resins used in this study D301 was commercial weakly basic resins (from Nankai University Chemical Plant).

2.2. Adsorbent preparation

Fe-D301 resin was prepared by soaking dry D301 resin in FeCl₃–HCl–NaCl solution (0.4 mol·dm^{−3} FeCl₃, 2.0 mol·dm^{−3} NaCl and 0.2 mol·dm^{−3} HCl) for 72 h at 298 K. The mixture was then filtered and rapidly added dropwise to a NaOH–NaCl solution (2.5 mol·dm^{−3} NaOH and 1.0 mol·dm^{−3} NaCl) to form Fe-D301. The Fe-D301 resin was filtered

☆ Supported by the National Natural Science Foundation of China (No. 21276027) and the Higher Educational Science and Technology Program of Shandong Province, China (NoJ14LC05).

* Corresponding author at: Department of Chemical Engineering, Binzhou University, Binzhou 256603, China. Tel./fax: +86 5433190097.

E-mail address: lichanghai2000@163.com (C.H. Li).

and washed with ethanol until no brown floc appeared, and then washed with distilled water until the pH was neutral. Finally, it was dried at 313 K for 24 h and stored in an airtight container [13]. Physical

Table 1
Physical properties of D301 and Fe-D301

Properties	D301	Fe-D301
Polymer matrix	Styrene-DVB	Styrene-DVB
Function group	-N(CH ₃) ₂	-N(CH ₃) ₂ + Fe-OH
Bead size/mm	0.35–0.55	0.35–0.55
Specific surface area/m ² ·g ⁻¹	29.5	35.8
Pore diameter/nm	20.5	17.5

properties of D301 and Fe-D301 listed in Table 1.

2.3. Analytical methods

The concentration of NSA, sulfuric acid and sulfurous acid in each solution were determined by a high-performance liquid chromatograph (LC-10AT, Shimadzu Corp., Kyoto, Japan) and a UV-Vis spectrophotometer (10A VP, Shimadzu Corp., Kyoto, Japan). Separation was performed on a C18 analytical column (150 mm × 4.6 mm i.d., particle size 5 μm). The mobile phase was methanol–water (50/50, v/v) containing 0.5 % KH₂PO₄ as pH regulator. The mobile phase flow rate was 0.8 cm³·min⁻¹, and the detector wavelength was 275 nm.

2.4. Adsorption studies

A single-solute adsorption on Fe-D301 resin was obtained for each solute dissolved in water. A series of 200 ml test flasks were filled with 100 ml of NSA, sulfuric acid and sulfurous acid solutions of varying initial concentration at pH < 4 and 298 K. Fe-D301 resin (0.1 g) was then added into each test flask and agitated intermittently for 24 h. The initial concentration of NSA was 0.1, 0.2, 0.3, 0.5, 0.7, 0.9, 1.0 g·dm⁻³ respectively. It was observed that adsorption equilibrium was reached in about 24 h on an orbit shaker revolving at 250 r·min⁻¹. Single-solute adsorptions for NSA, sulfuric acid and sulfurous acid were carried out in twice and three times, respectively.

The bisolute systems of NSA/sulfuric acid, NSA/sulfurous acid and sulfuric acid/sulfurous acid with different initial concentrations were prepared by mixing solutions of the same concentration in 1:1 volume ratio into a 100 ml solution. We performed bisolute adsorption experiments for the various initial concentrations with the fixed amount Fe-D301 resin (0.1 g) by following the same procedure as the single-solute adsorption experiment.

A trinary-solute system of NSA/sulfuric acid/sulfurous acid with different initial concentrations were prepared by mixing solutions of the same concentration in 1:1:1 volume ratio into a 100 ml solution. We performed trinary-solute adsorption experiments for the various initial concentrations with the fixed amount Fe-D301 resin (0.1 g) by following the same procedure as the single-solute adsorption experiment. During our experiments, three parallel measurements were performed for each process variable, and an average value is given. The maximum standard deviation of each triplicate data is 0.21 %, and the minimum is 0.14 %.

The adsorbed Phase concentration was calculated according to

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

Where C_0 and C_e are the initial and equilibrium concentration (mg·dm⁻³) of solute in solution, respectively; and V and W are the test solution volume (dm³) and mass (g) of adsorbent used for the test, respectively.

3. Single and Multisolute Competitive Adsorption Models

The adsorption isotherms employed frequently for single-solute systems are the 2-Parameter Langmuir and Freundlich models. The Langmuir and Freundlich models obey the correct thermodynamic boundary condition of Henry's law over an infinitely dilute concentration range. The Langmuir and Freundlich models for liquid-phase adsorption are written respectively as follows.

$$q_e = \frac{q_{\max} b C_e}{1 + b C_e} \quad (2)$$

$$q_e = k C_e^{\frac{1}{n}} \quad (3)$$

To analyze multisolute competitive adsorption behavior, the non-ideal competitive adsorbed model (NICM) [14] is used in this study. The equivalence of spreading π in a mixture containing N solutes leads to

$$a_i^l = z_i a_i^0 \quad (4)$$

$$\sum_{i=1}^N z_i = 1 \quad (5)$$

$$\frac{1}{a_i^s} = \sum_i \frac{z_i}{a_i^{s,0}} \quad (6)$$

$$a_i^s = z_i a_i^{s,0} \quad (7)$$

$$\frac{\pi A}{RT} = \int_0^{a_1^0} \frac{a_1^{s,0}(a_1^0)}{a_1^0} da_1^0 = \int_0^{a_2^0} \frac{a_2^{s,0}(a_2^0)}{a_2^0} da_2^0 = \dots \int_0^{a_i^0} \frac{a_i^{s,0}(a_i^0)}{a_i^0} da_i^0 \quad (8)$$

$$a_i^{s,0} = f(a_i^0, T) \quad (9)$$

among of them

$$a_i^l = \gamma_i^l c_{e,i} \quad (10)$$

$$a_i^s = \gamma_i^s q_{e,i} \quad (11)$$

$$a_i^0 = \gamma_i^{l,0} c_{e,i}^0 \quad (12)$$

$$a_i^{s,0} = \gamma_i^{s,0} q_{e,i}^0 \quad (13)$$

Where Davies empirical equation is applied to calculate $\gamma_i^l, \gamma_i^{l,0}$ [14], and Wilson equation is applied to calculate $\gamma_i^s, \gamma_i^{s,0}$ [14].

The NICM method is formulated on the basis that at equilibrium, the spreading pressures for all species are the same. A Newton-Raphson iteration method was used to solve these equations.

4. Results and Discussion

4.1. Single-solute adsorption equilibrium

The experiments of single-solute adsorption of NSA, sulfuric acid and sulfurous acid were run using Fe-D301 resin as an adsorbent. Adsorption equilibrium isotherms for sulfuric acid and NSA are shown in Fig. 1.

Three acids exhibited isotherms of type I [15]. Such isotherms were characteristic of strong adsorbate and adsorbent interactions. The 2-parameter Langmuir and Freundlich models were fitted to the adsorption data of each solute using the regression method. Fitted curves of the Langmuir and Freundlich models were shown in Fig. 1 for comparison with the adsorption data, and the parameters of both adsorption models were tabulated in Tables 2 and 3,

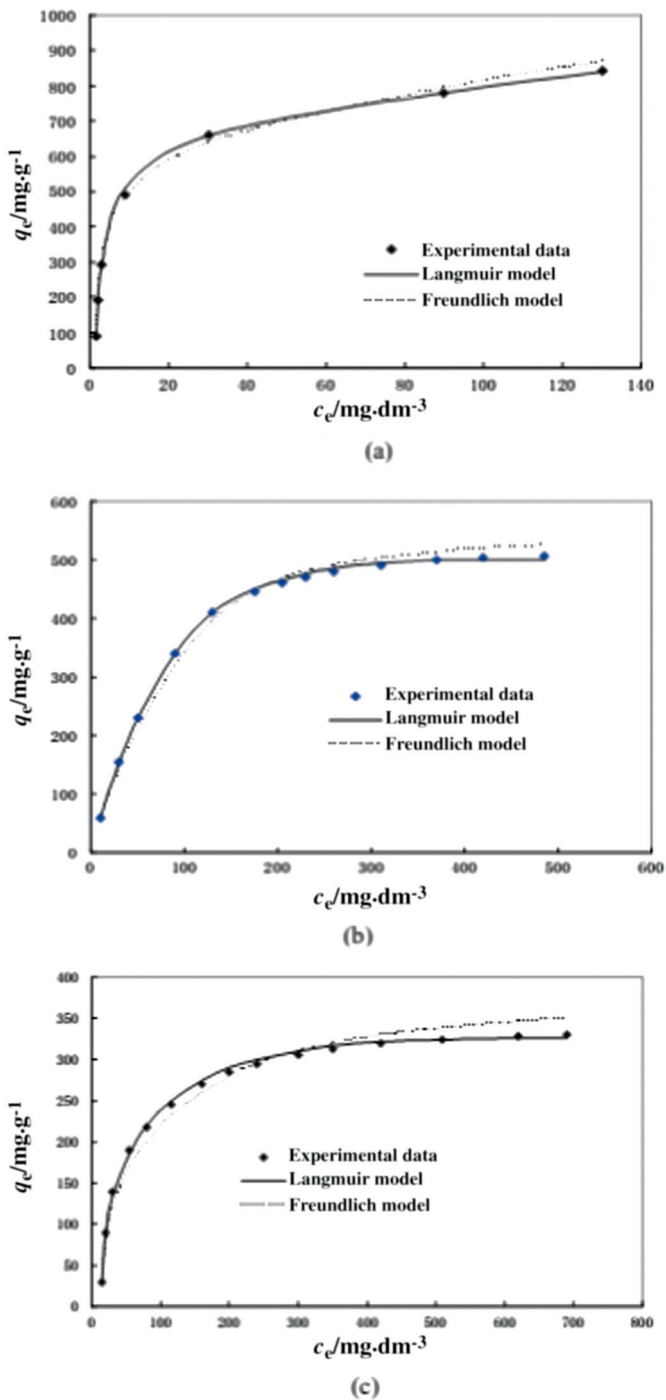


Fig. 1. Single-solute adsorption equilibrium isotherms of NSA, H₂SO₄ and H₂SO₃ on Fe-D301 resin(a)NSA, (b)H₂SO₄, (c)H₂SO₃, (initial concentration = 100–1000mg·dm^{−3}, solution = 0.1dm³, adsorbent = 0.1g,temperature = 298K)

respectively. The values of the parameter $q_{\max}$ in the Langmuir model, roughly reflected the order of adsorption affinity between the three acids.

Table 2
Langmuir parameters of each solute on Fe-D301 resin (298K)

Solute	$q_{\max}/\text{mg}\cdot\text{g}^{-1}$	$b/\text{g}\cdot\text{mg}^{-1}$	a	R^2
NSA	844	0.18	152	0.998
H ₂ SO ₄	548	0.024	13.2	0.999
H ₂ SO ₃	344	0.023	7.92	0.999

Table 3
Freundlich parameters of each solute on Fe-D301 resin (298K)

Solute	$\ln k$	$1/n$	R^2
NSA	5.211	0.353	0.926
H ₂ SO ₄	3.877	0.418	0.977
H ₂ SO ₃	2.826	0.504	0.834

The NSA, sulfuric acid and sulfurous acid onto Fe-D301 resin were attributed to interact with three acids and active sites of the adsorbent surface. Fe-D301 resin had two distinctly different active sites within the polymer phase. Firstly, covalently attached tertiary ammonium(-N(CH₃)₂) functional groups bound to the polymeric matrix of the host resin with high affinity toward hydrophobic anions such as sulfuric acid and so on. Secondly, surface iron oxyhydroxide particles have high affinity toward ligands with NSA. These two classes of adsorption sites were also independent of each other, and the amount of active sites of iron oxyhydroxide particles was much morn than that of tertiary ammonium(-N(CH₃)₂) functional groups on surface due to precipitating ferric onto resin surface.

Which solutes were adsorbed onto Fe-D301 resin, it could be explained with protonated theory of -N(CH₃)₂ functional group [16,17] and coordinate bonding between solutes and iron oxyhydroxide particles [18]. Among of these two attractive forces, the coordinate bonding dominated. So Fe-D301 resin exhibited the higher selective sorption toward NSA, which was mainly due to the coordinate bonding between Fe(III) and NSA. During the adsorption run, Note that in the pH range of no more than 4.0, NSA got selectively adsorbed through the formation of inner-sphere complexes [19], while other sulfuric and sufurous ions present in the solution form mainly outer-sphere complexes with protonated -N(CH₃)₂ functional group through electrostatic interactions and yielded poor sorption affinities. As a result, the adsorption affinity of NSA on Fe-D301 was found to be much higher than that of sulfuric and sufurous acids.

On the comparable of sulfurous acid, the capacity of sulfuric acid adsorbed onto Fe-D301 resin was higher than that of sulfurous acid. This resulted showed that the SO₄^{2−} which attached to two protonated sites of resin was expected to be more strongly anchored on the resin sites than SO₃^{2−}. The adsorption affinity of sulfuric acid on Fe-D301 was found to be much higher than that of sulfurous acid. This difference in behavior may be attributed to the weaker dissociation of SO₃^{2−} compared to SO₄^{2−} [20].

In view of the values of R^2 listed in Tables 2 and 3, the Langmuir model exhibited a little better fit to the adsorption data than the Freundlich model.

4.2. Bisolute competitive adsorption

Bisolute competitive adsorptions were performed for the NSA /sulfuric acid, NSA/sulfurous acid and sulfuric acid/ sulfurous acid binary system dissolved in water at 298K, respectively. The competitive adsorption data are shown in Fig. 2.

The $\wedge_{ij}$ parameter of NSA-H₂SO₄, NSA-H₂SO₃, H₂SO₄-H₂SO₃ was calculated with method of literature [14] on basis of adsorption data for the bisolute competitive adsorption, the results were tabulated in Table 4.

Fig. 2 showed adsorption data for the bisolute competitive adsorptions of NSA, sulfuric acid and sulfurous acid. Adsorption capacities of NSA (/sulfuric acid or /sulfurous acid) decreased when sulfuric acid and sulfurous acid were present due to the competition for the available sites between adsorbable components. NSA competitively displaced sulfuric acid and sulfurous acid from the limited adsorption sites available on Fe-D301 resin at higher concentrations. One of the main features of adsorption was that adsorption capacity of a solute was reduced when multiple solutes were present due to sharing the finite adsorption sites with other solutes on a competitive basis. The amount of decrease

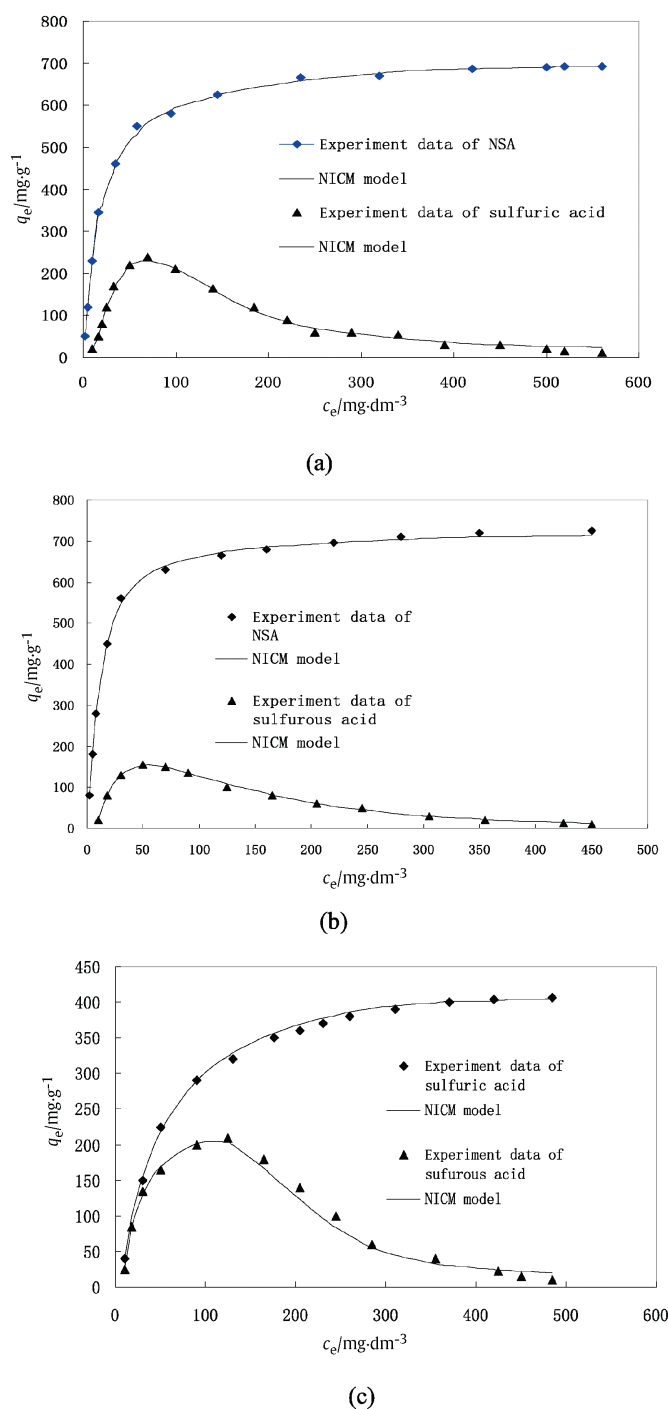


Fig. 2. Bisolute competitive adsorption behavior on Fe-D301 resin (a) NSA-H₂SO₄, (b) NSA-H₂SO₃, (c) H₂SO₄-H₂SO₃.

in adsorption capacity was found to be greater for sulfuric acid and sulfurous acid than for NSA, and it could be found that a dramatic decrease in adsorption capacity was observed for sulfurous acid at present of

Table 4

The $\hat{\gamma}_{ij}$ parameter of NSA-H₂SO₄, NSA-H₂SO₃, H₂SO₄-H₂SO₃

NSA (1) - H ₂ SO ₄ (2)		NSA (1) - H ₂ SO ₃ (3)		H ₂ SO ₄ (2) - H ₂ SO ₃ (3)	
$\hat{\gamma}_{12}$	$\hat{\gamma}_{21}$	$\hat{\gamma}_{13}$	$\hat{\gamma}_{31}$	$\hat{\gamma}_{23}$	$\hat{\gamma}_{32}$
3.635	0.389	3.915	0.696	2.006	0.557

sulfuric acid and NSA, which could be explained by protonated theory and coordinate bonding of Fe-D301 resin.

4.3. Multiple solute competitive adsorption models

To predict the competitive adsorptions, we applied NICM coupled with Langmuir adsorption model. The parameters of each model are listed in Tables 2 and 3.

Figs. 2 and 3 showed predictions from NICM coupled with Langmuir adsorption model. The NICM coupled with the single solute Langmuir model for NSA, sulfuric acid and sulfurous acid, respectively, provided the most favorable predictions for the bisolute and ternary-solute competitive adsorption of the acids on Fe-D301 resin.

5. Conclusions

Iron impregnation of D301 resin provided a suitable adsorbent for the removal of NSA, sulfuric acid and sulfurous acid from aqueous solution. Experiments on single-solute, bisolute and ternary-solute competitive adsorption equilibrium were carried out to investigate the adsorption behavior of NSA, sulfuric acid and sulfurous acid from solution at 298K onto Fe-D301 resin. Adsorptive affinity of the three acids on Fe-D301 resin was found to be in the order of NSA > sulfuric acid > sulfurous acid. The single-solute adsorption equilibria data were fitted to the Langmuir and the Freundlich adsorption models to obtain the model parameters. The NICM coupled with the single-solute adsorption models was used to predict the bisolute and ternary-solute competitive adsorption equilibrium. The NICM coupled with the Langmuir model for NSA, sulfuric acid and sulfurous acid, respectively, yielded the favorable representations of competitive adsorption behavior.

Nomenclature

A	surface area, m ² ·g ⁻¹
a_i^l	equilibrium activity of i solute in liquid, mg·dm ⁻³
a_i^s	equilibrium concentration of i solute in solid phase, mg·g ⁻¹
$a_i^{s,0}$	equilibrium activity of i solute in solid phase for single-solute adsorption, mg·g ⁻¹
a_i^0	equilibrium activity of i solute in liquid phase for single-solute adsorption, mg·dm ⁻³
a_T^s	total surface loading, mg·g ⁻¹
b	equilibrium constant, g·mg ⁻¹
c	final concentration in liquid phase, mg·dm ⁻³
c_e	equilibrium concentration in liquid, mg·dm ⁻³
$c_{e,i}$	equilibrium concentration of i solute in liquid, mg·dm ⁻³
$c_{e,i}^0$	equilibrium concentration of i solute in liquid phase for single-solute adsorption, mg·dm ⁻³
c^0	equilibrium concentration in liquid phase for single-solute adsorption, mg·dm ⁻³
c_0	initial concentration in liquid phase, mg·dm ⁻³
k	empirical Freundlich constant
N	number of components
n	empirical Freundlich constant
q	adsorbed phase concentration, mg·g ⁻¹
q_e	equilibrium concentration in solid phase, mg·g ⁻¹
$q_{e,i}$	equilibrium concentration of i solute in solid phase, mg·g ⁻¹
$q_{e,i}^0$	equilibrium concentration of i solute in solid phase for single-solute adsorption, mg·g ⁻¹
$q_{\max}$	saturation capacity, mg·g ⁻¹
q^0	equilibrium concentration in solid phase for single-solute adsorption, mg·g ⁻¹
R	gas constant, J·mol ⁻¹ ·K ⁻¹
T	temperature, K
V	test solution volume, dm ³
W	mass of sorbent, g
z	fraction on surface of the adsorbent
π	spreading pressure, g·s ⁻² ·mol ⁻¹

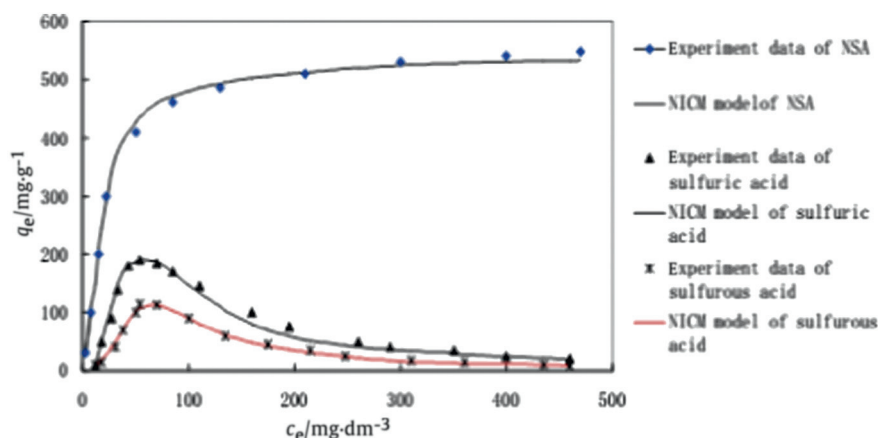


Fig. 3. Ternary-solute competitive adsorption models on Fe-D301 resin.

γ_i^l activity coefficient in liquid phase
 γ_i^s activity coefficient in solid phase
 $\gamma_i^{l,0}$ activity coefficient of i solute in liquid phase
 $\gamma_i^{s,0}$ activity coefficient of i solute in solid phase
 $\hat{\gamma}_{ij}$ is the adjustable parameter of Wilson model

References

- [1] C.H. Li, P.F.S. Hi, Treatment of 2-naphthalenesulfonic acid wastewater by the weakly basic resin, *Chem. Eng. J.* 29 (6) (2001) 42–45.
- [2] D.M. Jia, C.H. Li, B.L. Zhao, S. Sun, Studies on the adsorption of 2-naphthalenesulfonic acid on basic resin from effluents, *J. Chem. Eng. Data* 55 (2010) 5801–5806.
- [3] Y.L. Zhang, X.J. Yu, Q.L. Wang, Z.J. Jiang, T. Fang, Adsorption of zinc onto anionic ion-exchange resin from cyanide barren solution, *Chin. J. Chem. Eng.* 23 (4) (2015) 646–651.
- [4] M. Szlachta, V. Gerda, N. Chubar, Adsorption of arsenite and selenite using an inorganic ion exchanger based on Fe–Mn hydrous oxide, *J. Colloid Interface Sci.* 365 (2012) 213–221.
- [5] X. Ling, H.B. Li, H.W. Zha, C.L. He, J.H. Huang, Polar-modified post-cross-linked polystyrene and its adsorption towards salicylic acid from aqueous solution, *Chem. Eng. J.* 286 (2016) 400–407.
- [6] X.F. Jiang, J.H. Huang, Adsorption of Rhodamine B on two novel polar-modified post-cross-linked resins: Equilibrium and kinetics, *J. Colloid Interface Sci.* 467 (2016) 230–238.
- [7] G.Q. Xiao, R.M. Wen, Comparative adsorption of glyphosate from aqueous solution by 2-aminopyridine modified polystyrene resin, D301 resin and 330 resin: Influencing factors, salinity resistance and mechanism, *Fluid Phase Equilib.* 411 (2016) 1–6.
- [8] Z.W. Zhao, J.L. Zhang, X.Y. Chen, X.H. Liu, J.T. Li, W.G. Zhang, Separation of tungsten and molybdenum using macroporous resin: Equilibrium adsorption for single and binary systems, *Hydrometallurgy* 140 (2013) 120–127.
- [9] L.M. Camacho, R.R. Parra, S. Deng, Arsenic removal from groundwater by MnO₂-modified natural clinoptilolite zeolite: Effects of pH and initial feed concentration, *J. Hazard. Mater.* 189 (2011) 286–293.
- [10] H.B. Li, Z.Y. Fu, C. Yan, J.H. Huang, Y.N. Liu, S.I. Kirin, Hydrophobic–hydrophilic post-cross-linked polystyrene/poly (methyl acryloyl diethylenetriamine) interpenetrating polymer networks and its adsorption properties, *J. Colloid Interface Sci.* 63 (2016) 61–68.
- [11] M. Hadi, M.R. Samarghandi, G. McKay, Simplified fixed bed design models for the adsorption of acid dyes on novel pine cone derived activated carbon, *Water Air Soil Pollut.* 218 (2011) 197–212.
- [12] J. Wang, S. Zhang, B. Pan, W. Zhang, L. Lv, Hydrous ferric oxide–resin nanocomposites of tunable structure for arsenite removal: Effect of the host pore structure, *J. Hazard. Mater.* 198 (2011) 241–246.
- [13] D.M. Jia, Y.J. Li, C.H. Li, Iron-Impregnated weakly basic resin for the removal of 2-naphthalenesulfonic acid from aqueous solution, *J. Chem. Eng. Data* 56 (2011) 3881–3889.
- [14] C.H. Li, D.M. Jia, Separation of Organic/ Inorganic Mixed Acid Using Technology of Exchange Adsorption, Chemical Industrial Press, Beijing, 2015.
- [15] C.J. Radke, J.M. Prausnitz, Thermodynamics of multi-solute adsorption from dilute liquid solutions, *AIChE J.* 18 (4) (1972) 761–768.
- [16] W. Taktuji, H. Yoshida, Removal of organic acid from wine by adsorption on weakly base ion exchangers: Equilibria for sing and binary systems, *Sep. Sci. Technol.* 29 (11) (1994) 1473–1490.
- [17] V.M. Bhandari, V.A. Juvekar, Sorption of dibasic acid on weak base resins, *Ind. Eng. Chem. Res.* 32 (7) (1993) 200–213.
- [18] X. Li, K. He, B.C. Pan, Efficient As(III) removal by macroporous anion exchanger supported Fe–Mn binary oxide: Behavior and mechanism, *Chem. Eng. J.* 190 (2012) 131–138.
- [19] D.A. Dzombak, F.M.M. Morel, Surface Complexation Modeling: Hydrous Ferric Oxide, New York, Wiley, 1990.
- [20] H.J. Zheng, Z.Q. Li, S. He, Study on extraction process of lactic acid from fermentation broth with anionic resin, *Food Sci.* 30 (6) (2009) 84–88.