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Equilibrium Modeling of Ternary Adsorption of Metal Ions onto Rice Husk Ash

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The aim of the present study is to analyze the competitive adsorption of cadmium (Cd(II)), nickel (Ni(II)), and zinc (Zn(II)) ions onto rice husk ash (RHA) from ternary metal ion mixtures. RHA is a waste material obtained from the flue gas of the rice husk fired boilers. The equilibrium adsorption data were obtained at different initial concentrations ($C_0 = 10$ to $100\ \mathrm{mg \cdot dm^{-3}}$), 5 h contact time, 30 °C temperature, and RHA dosage of $10\ \mathrm{mg \cdot dm^{-3}}$ at pH = 6. The Freundlich and the Redlich−Peterson models represent the single ion equilibrium adsorption data better than the Langmuir model. The equilibrium metal removal decreases with increasing concentrations of the other metal ions, and the combined action of Cd(II), Ni(II), and Zn(II) ions on RHA is found to be antagonistic. The competitive Sheindorf−Rebuhn−Sheintuch (SRS) model fits the ternary adsorption equilibrium data satisfactorily.

1. Introduction

Much of the work on the adsorption of heavy metal ions by various kinds of adsorbents has focused on the uptake of single metals. Since industrial effluents generally contain several metals, it is necessary to study the simultaneous adsorption of two or more metals from aqueous solutions.[1] In multimetal adsorption, the adsorption of one metal ion, generally, interferes with that of another. Thus studies on adsorption of heavy metals from binary and ternary systems to quantify the interference of one metal on the adsorption of the other metal ions are very important. Cadmium (Cd(II)), nickel (Ni(II)), and zinc (Zn(II)) are among the most common metals found in the industrial effluents of many industries (e.g., from mine drainage, plating plants, paint and ink formulation units, and porcelain enamelling).

In wastewater treatment, activated carbon is regarded as one of the most effective adsorbents for the removal of metal ions from fluid streams. However, due to its high cost and about (10 to 15) % loss during regeneration, unconventional adsorbents like bagasse fly ash, rice husk ash (RHA), red mud, fly ash, baker′s yeast cells, alkaganeite, corncob, river bed sediments, animal bones, oil shale ash, etc. have attracted the attention of several investigators.[1−9] Rice husk is an agricultural waste, accounting for about one-fifth of the annual gross rice production (545 million metric tonnes) of the world.[10] Rice husk is used as a fuel in boiler furnaces by a number of industries, in India as well as other countries, to produce steam. The rice husk ash (RHA) carried by the flue gas is collected from the dust collection equipment attached upstream of the stacks of rice husk-fired boilers and furnaces. The amount of RHA generated is huge, and most industries spend money on its collection, transportation, and disposal as a landfill material. RHA has good adsorptive properties and has been used previously for the adsorptive removal of metal ions,[10−13] dyes,[14] and also for the removal of color from biodigester distillery effluent.[15] RHA is plentiful and is available free of cost from industries using rice husk fired furnaces/boilers. Its only cost will be on its collection, transportation to the point of utility, pretreatment like sieving, and final disposal. Thus, the adsorptive removal of metal ions with RHA may be much cheaper than that with activated carbons.

Adsorption from three-component or multicomponent mixtures covering the whole range of various parameters requires a large number of experiments to be conducted. Thus, only a few adsorption studies have been reported on the adsorption of metal ions from ternary metal ion solution. Designing an optimized adsorption system requires establishment of the best correlation which represents the equilibrium data. The equilibrium adsorption isotherm equations proposed for single-component adsorption (e.g., Langmuir, Freundlich, Redlich−Peterson (R−P)[16]) have been extended and modified to represent ternary and multicomponent adsorption equilibria. Some of the important multicomponent adsorption equilibrium models include nonmodified, modified, and extended-Langmuir models;[17,18] nonmodified and modified R−P models; and the Sheindorf−Rebuhn−Sheintuch (SRS) model.[19] Srivastava et al.[1,20,21] have discussed in detail the theory associated with these models.

The experimental data and the sorption isotherms for the adsorption of single and binary metal ions from aqueous solutions by RHA have been reported recently.[11,12,22] However, no information is available in the literature for the simultaneous removal of Cd(II), Ni(II), and Zn(II) ions by RHA. The aim of the present paper is to study the feasibility of using RHA as an adsorbent for the individual and simultaneous removal of Cd(II), Ni(II), and Zn(II) from aqueous solutions, to present the experimental equilibrium sorption data, and to examine the applicability of various multicomponent adsorption isotherm equations to the competitive adsorption equilibria of the metal ions (Cd(II), Ni(II), and Zn(II)) in a ternary system.

2. Experimental

2.1. RHA. RHA was used as obtained from a nearby paper mill (Barnala paper mill, Punjab, India) without any pretreatment for the removal of metal ions from synthetic aqueous solutions in a batch treatment process. Detailed physicochemical characteristics of the RHA have been presented elsewhere.[11,12]

2.2. Chemicals. All the chemicals used in the study were of analytical reagent grade. Cadmium sulfate octahydrate

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Table 1. Comparison of Individual Adsorption Equilibrium Uptakes and Yields of Cadmium(II), Nickel(II), and Zinc(II) Ion Adsorption onto Rice Husk Ash

$C_{o,Cd}$	$C_{e,Cd}$	$q_{e,Cd}$	Ad_{Cd} %	$C_{o,Ni}$	$C_{e,Ni}$	$q_{e,Ni}$	Ad_{Ni} %	$C_{o,Zn}$	$C_{e,Zn}$	$q_{e,Zn}$	Ad_{Zn} %
10	1.4	0.86	86	10	0.61	0.939	93.9	10	0.49	0.951	95.1
20	6.5	1.35	67.5	20	4.5	1.55	77.5	20	3.4	1.66	83
30	12.5	1.75	58.33	30	9.5	2.05	68.33	30	7.7	2.23	74.33
50	28.9	2.11	42.2	50	20.6	2.94	58.8	50	16	3.4	68
100	71.4	2.86	28.6	100	59.3	4.07	40.7	100	49.3	5.07	50.7

Table 2. Isotherm Parameters Values for the Removal of Cadmium(II), Nickel(II), and Zinc(II) Ions by Rice Husk Ash

Langmuir isotherm $q_e = q_m K_L C_e / 1 + K_L C_e$

adsorbate	K_L/dm^3·mg^{-2}	q_m/mg·g^{-1}	MPSD
Cd(II)	0.3477	2.3027	18.6659
Ni(II)	0.7109	2.6238	30.8346
Zn(II)	0.6644	3.0798	33.9572

Freundlich isotherm $q_e = K_F C_e^{1/n}$

adsorbate	K_F/(mg·g^{-1})(dm^3·mg^{-1})$^{-1/n}$	$1/n$	MPSD
Cd(II)	0.7772	0.3043	3.0220
Ni(II)	1.0295	0.3280	7.9947
Zn(II)	1.1396	0.3700	9.4881

Redlich−Peterson isotherm $q_e = K_R C_e / 1 + a_R C_e^{\beta}$

adsorbate	K_R/L·g^{-1}	a_R/dm^3·mg^{-1}	β	MPSD
Cd(II)	3419.4623	5265.9654	0.6481	8.0727
Ni(II)	18.4183	16.8939	0.6886	11.3007
Zn(II)	9357.4825	8210.1211	0.6301	11.6238

($3CdSO_4 \cdot 8H_2O$), zinc sulfate heptahydrate ($ZnSO_4 \cdot 7H_2O$), NaOH, HCl, HNO_3, H_2SO_4, and CH_3COOH were obtained from SD. Fine Chemicals, Mumbai, India. Nickel chloride hexahydrate ($NiCl_2 \cdot 6H_2O$) was procured from Qualigens Fine Chemicals, Mumbai. Stock solutions of 1 g·dm^{-3} strength of Cd(II), Ni(II), and Zn(II) were prepared by dissolving an exact amount of $3CdSO_4 \cdot 8H_2O$, $NiCl_2 \cdot 6H_2O$, and $ZnSO_4 \cdot 7H_2O$ separately in double-distilled water (DDW). The stock solution for each metal salt was appropriately diluted with DDW to give metal ion concentrations in the range of (10 to 100) mg·dm^{-3} for use in the experiments.

The concentration of Cd(II), Ni(II), and Zn(II) ions in the aqueous samples was determined using a flame atomic absorption spectrophotometer (GBC Avanta, Australia) with a detection limit of (0.009, 0.040, and 0.008) mg·dm^{-3} at the wavelength of 228.8 nm, 232 nm, and 213.9 nm, for Cd(II), Ni(II), and Zn(II), respectively, by using an air-acetylene flame. Metal ion concentrations were determined with reference to the appropriate standard metal ion solutions.

2.3. Batch Adsorption Studies. For each experimental run, 0.1 dm^{-3} aqueous solutions of a known concentration of Cd(II), Ni(II), Zn(II), or a ternary mixture of these components was taken in a 0.25 dm^{-3} conical flask containing 1 g of RHA. These flasks were agitated at a constant shaking rate of 150 rpm in a temperature-controlled orbital shaker (Remi Instruments, Mumbai) maintained at 30 °C. For single metal−RHA systems, the initial metal ion concentration was varied in the range of (10 to 100) mg·dm^{-3}. In ternary metal ion aqueous solution−RHA systems, the Ni(II) and Zn(II) concentrations were varied in the range of (10 to 100) mg·dm^{-3} (viz., (10, 20, 30, 50, and 100) mg·dm^{-3}) at each initial concentration of Cd(II) solution: viz., (10, 20, 30, 50, and 100) mg·dm^{-3}. In all the experiments of the present study, the pH of the solution was maintained at 6, and a buffer system of potassium dihydrogen orthophosphate (KH_2PO_4) and sodium hydroxide (NaOH) was used. This buffer was made by mixing 0.1 dm^{-3} of 0.1 M KH_2PO_4 with 0.0112 dm^{-3} of 0.1 M NaOH. A significant buffering capacity was achieved at pH 6 using this buffer with $a < 5$ % average deviation from the adjusted pH value.

3. Results and Discussion

3.1. Monocomponent Adsorption of Metal Ions. The equilibrium sorption uptake of any metal ion ($q_{e,i}$), individual adsorption yield (Ad_i %) and total adsorption yields (Ad_{Tot} %) have been calculated by using the following equations

$$q_{e,i} = (C_{0,i} - C_{e,i})V/w, \text{(mg of adsorbate per g of adsorbent)} \tag{1}$$

$$Ad_i\ \% = 100(C_{0,i} - C_{e,i})/C_{0,i} \tag{2}$$

$$Ad_{Tot}\ \% = 100 \sum (C_{0,i} - C_{e,i}) / \sum C_{0,i} \tag{3}$$

where V is the volume of the adsorbate containing solution (dm^{-3}) and w is the mass of the adsorbent (g).

The equilibrium uptake and the adsorption yield obtained for a single component (Cd(II) or Ni(II) or Zn(II)) solution is shown in Table 1. It may be seen from the table that when the initial ion concentration increases from 10 mg·dm^{-3} to 100 mg·dm^{-3} the loading capacity of RHA increases from 0.86 mg·g^{-1} to 2.86 mg·g^{-1} for Cd(II); from 0.94 mg·g^{-1} to 4.07 mg·g^{-1} for Ni(II); and from 0.95 mg·g^{-1} to 5.07 mg·g^{-1} for Zn(II). The initial concentration provides the necessary driving force to overcome the resistances to the mass transfer of Cd(II), Ni(II), and Zn(II) ions between the aqueous phases and the solid phase. It also enhances the interaction between the metal ions in the aqueous phase and the RHA. Therefore, an increase in the initial concentration of metal ions in the aqueous phase enhances the adsorptive uptake of Cd(II), Ni(II), and Zn(II) ions.

3.2. Monocomponent Adsorption Isotherm. Various isotherm equations like those of Freundlich, Langmuir, and R−P have been used to describe the monocomponent equilibrium characteristics of adsorption of individual ions onto RHA. The adsorption parameters for each metal ion obtained from the fitting of different isotherm models with the experimental data are listed in Table 2 along with the MPSD values. The MPSD error values are least for the Freundlich model followed by the R−P and Langmuir models. Therefore, the equilibrium adsorption data of Cd(II), Ni(II), and Zn(II) ion adsorption on RHA can be represented appropriately by the Freundlich model in the studied concentration range. RHA has a heterogeneous surface. It is, therefore, expected that the Freundlich and R−P isotherm equations can better represent the equilibrium sorption data than the Langmuir isotherm model.

The single-component Freundlich constants, K_F and $1/n$, indicate the adsorption capacity and adsorption intensity, respectively. The value of $1/n$ determines the nonlinearity of the adsorption isotherm. The higher the value of the exponent $1/n$, the higher the affinity and the heterogeneity of the adsorbent sites will be. With $1/n$ lower than 0.1, the adsorption approaches a so-called rectangular or irreversible isotherm condition. Since $1/n < 1$, all the metal ions are favorably adsorbed by RHA. It is found from Table 2 that the RHA shows greater heterogeneity for Zn(II) than that for Ni(II) and Cd(II). The K_F values indicate

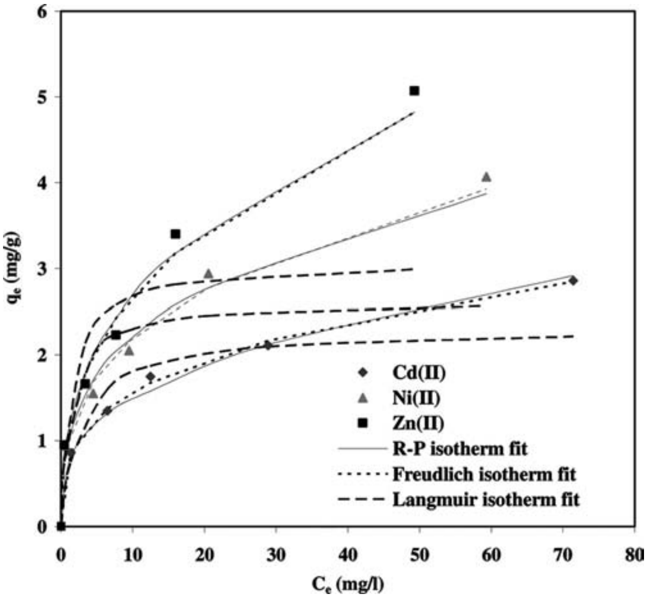

Figure 1. Equilibrium adsorption isotherms for individual adsorption of Cd(II), Ni(II), and Zn(II) ion adsorption onto rice husk ash. Experimental data points given by the symbols and the lines predicted by the Langmuir, Freundlich, and Redlich−Peterson models.

the higher uptake of Zn(II) by RHA followed by Ni(II) and Cd(II). The adsorption capacity of the RHA for the metal ions was in the order: Zn(II) > Ni(II) > Cd(II). This trend is according to the increasing size of the metal ions: Zn(II) (1.53 Å) < Ni(II) (1.62 Å) < Cd(II) (1.71 Å). Smaller sized metal ions have better accessibility to the surface and pores than the bigger sized metal ions, resulting in a higher adsorption capacity of the smaller sized metals ions.[21,22]

The value of the R−P constant β between 0 and 1 indicates favorable adsorption. The comparison of the experimental and predicted equilibrium uptake (q_e) from the single-component Freundlich and R−P models for the individual adsorption of Cd(II), Ni(II), and Zn(II) from the aqueous solution of different concentrations onto RHA is presented in Figure 1. Either one of the models could be used to represent the experimental equilibrium sorption data.

3.3. Ternary Sorption of Metal Ions. A total of 125 experiments were conducted to check the effect of initial concentration of metal ions (Cd(II), Ni(II), and Zn(II)) with respect to each other for the initial metal ion concentrations of (10, 20, 30, 50, and 100) $\text{mg}\cdot\text{dm}^{-3}$. Representative sorption equilibrium data are shown in Table 3. The individual and total adsorption equilibrium uptakes by RHA and the yields of Cd(II), Ni(II), and Zn(II) ions at various initial concentrations of metal ions are listed in Table 3. It was found that the equilibrium Cd(II) uptake increases with an increase in the initial Cd(II) concentration up to 100 $\text{mg}\cdot\text{dm}^{-3}$ for the same concentrations of Ni(II) and Zn(II) ions in the solution. The equilibrium uptake of Cd(II), however, decreases with an increase in Ni(II) and Zn(II) ion concentrations.

In general, an increase in the initial Ni(II) and/or Zn(II) ion concentration decreases the individual sorption yield and equilibrium uptake of Cd(II) and the total adsorption yield for each experimental run. At 100 $\text{mg}\cdot\text{dm}^{-3}$ initial Cd(II) ion concentration and in the absence of Ni(II) and Zn(II) ions, the adsorbed Cd(II) ions at equilibrium is found to be 2.86 $\text{mg}\cdot\text{g}^{-1}$ (Table 1). However, in the presence of 100 $\text{mg}\cdot\text{dm}^{-3}$ Ni(II) ion concentration and 10 $\text{mg}\cdot\text{dm}^{-3}$ Zn(II) ion concentration, the total uptake of Cd(II) ion at its initial concentration of 100 $\text{mg}\cdot\text{dm}^{-3}$ was only 2.01 $\text{mg}\cdot\text{g}^{-1}$. A further increase in initial concentration of Ni(II) and Zn(II) ions to 100 $\text{mg}\cdot\text{dm}^{-3}$ both each decreased the uptake of Cd(II) ion to 0.60 $\text{mg}\cdot\text{g}^{-1}$ only. Therefore, the effect of the ternary mixture is less than that of the sum of each of the individual adsorbates in the mixture, i.e., the combined effect of the three components, viz., Cd(II), Ni(II), and Zn(II), seems to be antagonistic.

Table 3. Comparison of Individual and Total Adsorption Equilibrium Yields at Different Cadmium(II) Concentrations in the Presence of Increasing Concentrations of Nickel(II) and Zinc(II) Ions onto Rice Husk Ash

$C_{o,Cd}$	$q_{e,Cd}$	Ad_{Cd} %	$C_{o,Ni}$	$q_{e,Ni}$	Ad_{Ni} %	$C_{o,Zn}$	$q_{e,Zn}$	Ad_{Zn} %	Ad_{Tot} %
10	0.76	76.39	10	0.80	79.85	10	0.83	83.37	79.87
10	0.70	70.09	100	3.50	34.97	10	0.49	49.19	39.08
10	0.46	46.00	10	0.46	45.50	100	4.57	45.66	45.67
10	0.44	43.90	20	0.89	44.32	100	4.03	40.31	41.20
10	0.39	38.80	30	1.07	35.77	100	3.67	36.70	36.65
10	0.36	36.27	50	1.53	30.54	100	3.31	33.07	32.48
10	0.32	31.97	100	1.74	17.39	100	2.63	26.30	22.32
20	1.29	64.64	10	0.79	78.95	10	0.82	82.04	72.57
20	1.17	58.75	100	3.62	36.16	10	0.46	45.74	40.37
20	0.75	37.26	10	0.47	46.87	100	4.15	41.54	41.29
20	0.63	31.31	20	0.78	38.96	100	4.18	41.77	39.87
20	0.57	28.37	30	0.99	33.14	100	4.14	41.35	37.98
20	0.43	21.64	50	1.39	27.84	100	3.40	33.99	30.73
20	0.33	16.49	100	1.78	17.85	100	2.62	26.17	21.51
30	1.79	59.54	10	0.78	78.42	10	0.80	80.45	67.50
30	1.69	56.18	100	3.09	30.87	10	0.46	45.61	37.35
30	1.05	35.01	10	0.44	44.48	100	4.46	44.59	42.53
30	0.97	32.37	20	0.77	38.37	100	4.29	42.89	40.19
30	0.88	29.31	30	0.93	30.97	100	4.04	40.45	36.58
30	0.78	26.02	50	1.04	20.83	100	3.43	34.33	29.19
30	0.65	21.58	100	1.22	12.21	100	1.93	19.32	16.53
50	2.21	44.25	10	0.79	78.64	10	0.79	78.76	54.10
50	2.08	41.68	100	3.18	31.76	10	0.41	41.01	35.44
50	1.34	26.86	10	0.48	47.59	100	4.51	45.08	39.54
50	1.19	23.81	20	0.68	34.23	100	4.09	40.87	35.07
50	1.00	19.95	30	0.72	24.14	100	3.80	38.03	30.69
50	0.75	15.07	50	0.88	17.53	100	3.19	31.94	24.12
50	0.55	10.94	100	0.84	8.45	100	1.56	15.56	11.79
100	2.57	25.70	10	0.78	77.98	10	0.79	78.57	34.46
100	2.01	20.10	100	2.98	29.75	10	0.40	39.73	25.63
100	1.12	11.19	10	0.46	45.70	100	4.32	43.22	28.08
100	0.99	9.90	20	0.58	28.96	100	3.92	39.24	24.97
100	0.82	8.19	30	0.66	21.87	100	3.68	36.80	22.42
100	0.78	7.83	50	0.72	14.46	100	3.25	32.50	19.02
100	0.60	5.99	100	0.64	6.36	100	1.07	10.74	7.69

Using Table 1, it was expected that the total sorption yield must be equal to 40 % for the total metal concentration of 300 $\text{mg}\cdot\text{dm}^{-3}$ containing equal (100 $\text{mg}\cdot\text{dm}^{-3}$) concentrations of Cd(II), Ni(II), and Zn(II) in the mixture [Ad_{Tot} % = 40 = 100·[(28.6 $\text{mg}\cdot\text{dm}^{-3}$ Cd(II) + 40.7 $\text{mg}\cdot\text{dm}^{-3}$ Ni(II) + 50.7 $\text{mg}\cdot\text{dm}^{-3}$ Zn(II) ion)/300 $\text{mg}\cdot\text{dm}^{-3}$ initial total concentration]]. However, the total experimental sorption yield was 7.69 % for total metal ion concentration of 300 $\text{mg}\cdot\text{dm}^{-3}$ consisting of 100 $\text{mg}\cdot\text{dm}^{-3}$ each of Cd(II), Ni(II), and Zn(II) ions [Ad_{Tot} % = 7.69 = 100·[(5.99 $\text{mg}\cdot\text{dm}^{-3}$ Cd(II) + 6.36 $\text{mg}\cdot\text{dm}^{-3}$ Ni(II) + 10.74 $\text{mg}\cdot\text{dm}^{-3}$ Zn(II) ion)/300 $\text{mg}\cdot\text{dm}^{-3}$ initial total concentration]]. This shows that the ternary metal ion solution exhibited inhibitory (antagonistic) sorption for each metal, thereby resulting in a lower sorption yield.

3.4. Multicomponent Adsorption Models. The simultaneous sorption data of Cd(II), Ni(II), and Zn(II) from the ternary mixture onto RHA have been fitted to the multicomponent isotherm models, viz., nonmodified, modified, and extended Langmuir models; nonmodified and modified R−P models; and the SRS model. These equations are given in Table 4. Isotherm parameters of these models were found by using MS Excel 2002 for Windows by minimizing the modified form of Marquardt′s percent standard deviation (MPSD)[23] that has been extensively

Table 4. Ternary Equilibrium Isotherm Parameters for the Simultaneous Removal of Cd(II), Ni(II), and Zn(II) Metal Ions for the Rice Husk Ash

nonmodified Langmuir model		nonmodified R−P model	
$q_{e,i} = (q_{m,i}K_{L,i}C_{e,i})/(1 + \sum_{j=1}^{N} K_{L,j}C_{e,j})$		$q_{e,i} = (K_{R,i}C_{e,i})/1 + \sum_{j=1}^{N} a_{R,j}C_{e,j}^{\beta,j})$	
MPSD	114.12	MPSD	139.99

modified Langmuir model		extended-Langmuir model	
$q_{e,i} = [q_{m,i}K_{L,i}(C_{e,i}/\eta_{L,i})]/[1 + \sum_{j=1}^{N} K_{L,j}(C_{e,j}/\eta_{L,j})]$		$q_{e,i} = (q_{\max} K_{EL,i}C_{e,i})/(1 + \sum_{j=1}^{N} K_{EL,j}C_{e,j})$	
adsorbate	$\eta_{L,i}$	$K_{EL,i}$	$q_{\max}$
Cd(II)	4.371	0.040	3.562
Ni(II)	0.660	0.643	
Zn(II)	0.555	1.016	
MPSD	101.70	102.65	

SRS model				modified R−P model
$q_{e,i} = K_{F,i}C_{e,i}(\sum_{j=1}^{N} a_{ij}C_{e,j})^{(1/n_i)}-1$				$q_{e,i} = [K_{R,i}(C_{e,i}/\eta_{R,i})]/[1 + \sum_{j=1}^{N} a_{R,j}(C_{e,j}/\eta_{R,j})^{\beta,j}]$
adsorbate	a_{ij}	a_{ij}	a_{ij}	$\eta_{R,i}$
Cd(II)	1	0.010	4.442	6.936
Ni(II)	0.010	1	3.282	0.001
Zn(II)	0.010	2.991	1	2.590
MPSD	82.245			127.807

used for single-component isotherm modeling.[11,12,14] However, for multicomponent adsorption, the MPSD error function was modified as follows to test the adequacy and accuracy of various multicomponent isotherm models

$$\mathrm{MPSD} = 100\sqrt{\frac{1}{n_m - n_p}\sum_{i=1}^{n_m}\left(\frac{\left(\sum_{i=1}^{N} q_{e,i,\exp}\right) - \left(\sum_{i=1}^{N} q_{e,i,\mathrm{cal}}\right)}{\sum_{i=1}^{N} q_{e,i,\exp}}\right)_i^2} \tag{4}$$

In the above equation, the subscripts "exp" and "cal" show, respectively, the experimental and calculated values; and n_m is the number of measurements; n_p is the number of parameters in the model; and N is the number of adsorbates ($N = 3$ for the present case). For $N = 1$, this equation reduces to the error function as used for single-component isotherm modeling. Hence, it is clear that the summations given within braces in the numerator and denominator of eq 4 relate to the total concentrations of metals sorbed, both experimental and predicted, in the solid phase.

The parametric values of all the multicomponent sorption models are given in Table 4. The MPSD values between the experimental and calculated q_e values for the entire data set of Cd(II), Ni(II), and Zn(II) are also given in Table 4. A comparison of MPSD values for different isotherm models shows that the metal ion sorption from a ternary system showed MPSD values of 82.25 for the fitting of the experimental data to the SRS model. This MPSD value was the lowest in comparison to other models. Therefore, the SRS model best-

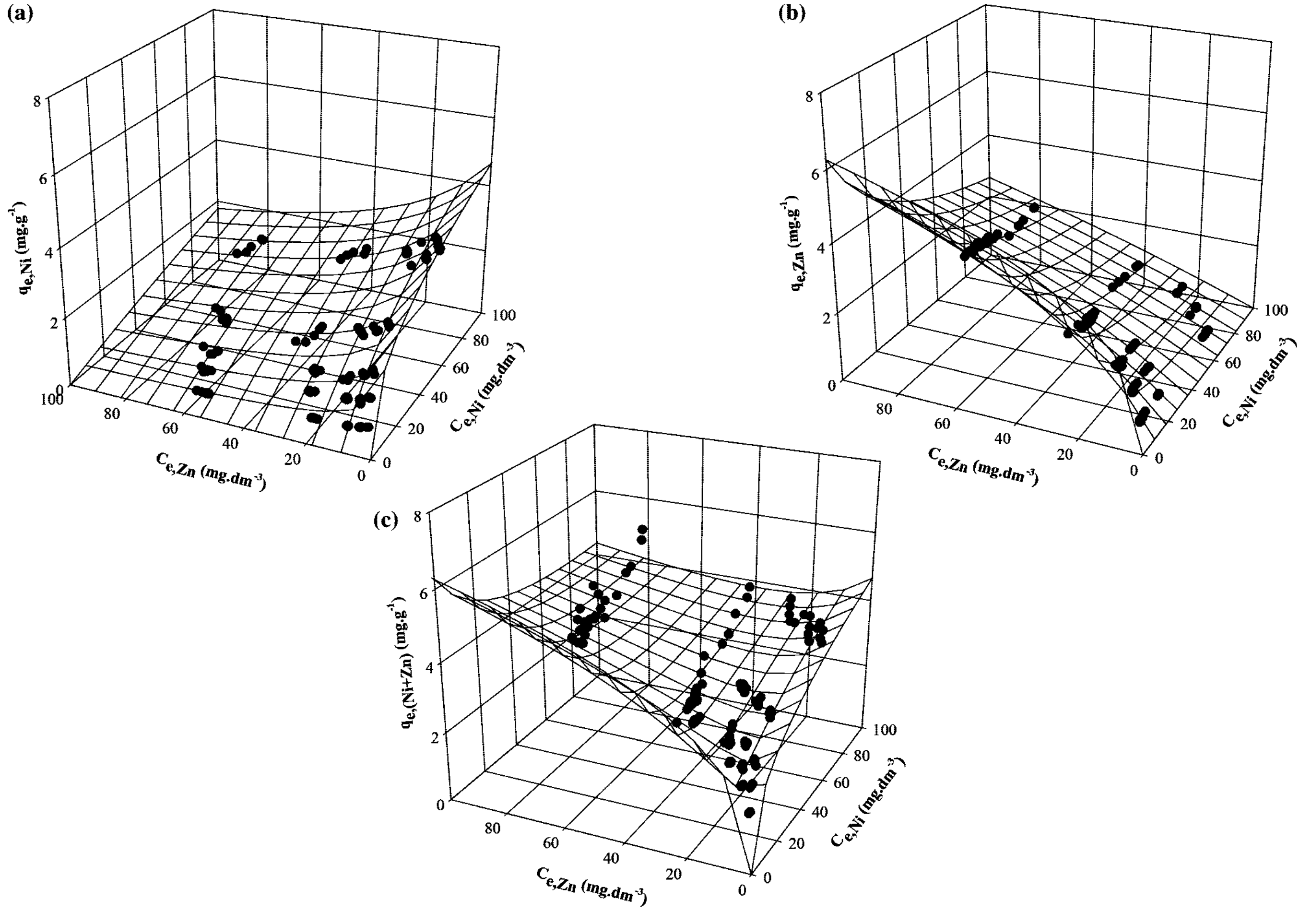

Figure 2. Three-dimensional adsorption isotherm surfaces created by using a multicomponent SRS model for the Cd(II) + Ni(II) + Zn(II) systems with $C_{e,Cd}$ as a parameter. (a) The effect of Zn(II) concentration on the equilibrium uptake of Ni(II); (b) the effect of Ni(II) concentration on the equilibrium uptake of Zn(II); (c) the effect of Ni(II) and Zn(II) concentration on the equilibrium total uptake of Ni(II) + Zn(II) ions by RHA.

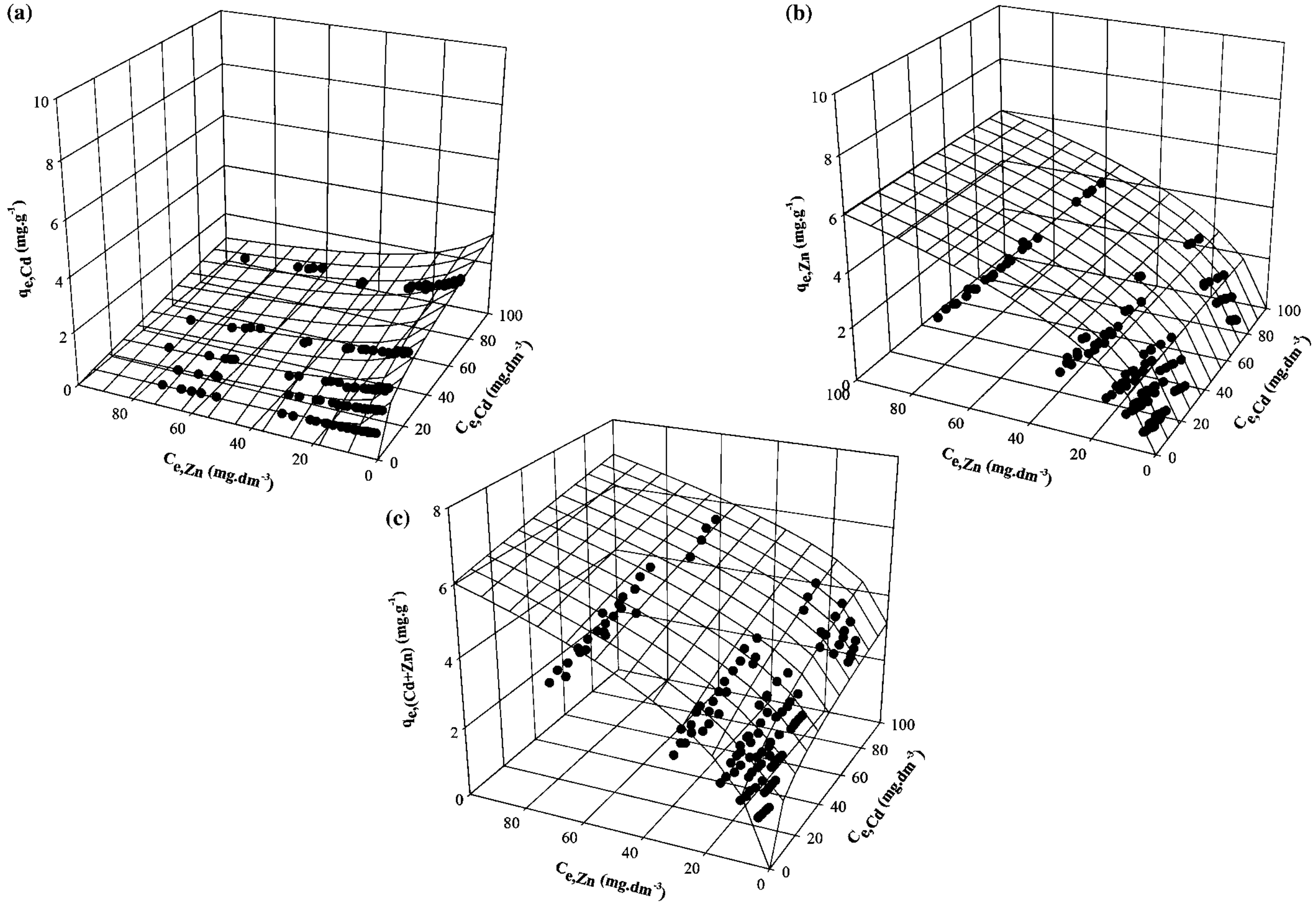

Figure 3. Three-dimensional adsorption isotherm surfaces created by using a multicomponent SRS model for the Cd(II) + Ni(II) + Zn(II) systems with $C_{e,Ni}$ as a parameter. (a) The effect of Zn(II) concentration on the equilibrium uptake of Cd(II); (b) the effect of Cd(II) concentration on the equilibrium uptake of Zn(II); (c) the effect of Cd(II) and Zn(II) concentration on the equilibrium total uptake of Cd(II) + Zn(II) ions by RHA.

fitted the experimental sorption data of the metal ions from the ternary systems in comparison to the other models.

The multicomponent nonmodified Langmuir model shows a poor fit to the experimental data with an MPSD value of 114.12. However, the use of the interaction term, modified Langmuir coefficient ($\eta_{L,i}$), improved the fit of the modified Langmuir model as indicated by the lowered MPSD value (101.70). The multicomponent extended-Langmuir model has been found to adequately describe the sorption equilibria of the ternary system of Cr(VI), Cu(II), and Cd(II) for a biosorbent *R. arrhizus*.[24] However, MPSD values for this model are large in the present study. The overall total metal ion uptake (q_{max}) by RHA is 3.562 mg·g^{-1}. This value is considerably lower than the sum of the equilibrium uptake of Cd(II), Ni(II), and Zn(II) ions resulting from the single-component sorption systems. For that reason, the sorption sites of Cd(II), Ni(II), and Zn(II) in ternary systems onto RHA may likely be partially overlapped. It may also imply that there may be a variety of binding sites on the sorbents showing partial specificity for the individual metal ions. The information obtained from the equilibrium uptakes seems to violate the basic assumptions of the Langmuir model; i.e., the entire adsorbent surface is homogeneous and there is no lateral interaction between the adsorbate molecules, and thus the affinity of each binding site for the adsorbate molecules should be uniform.[25] The $K_{EL,i}$ values reflect the affinity between the adsorbent and the metals in the ternary systems. In the present study, the $K_{EL,i}$ values are 0.123 dm^3·mg^{-1} for Cd(II), 0.257 dm^3·mg^{-1} for Ni(II), and 0.202 dm^3·mg^{-1} for Zn(II). The nonmodified R–P model gave very high MPSD values; however, the modified R–P model improved the fit considerably.

The multicomponent SRS model applies to systems where each component individually obeys the single-component Freundlich isotherm. The competition coefficients, a_{ij}, in the SRS model describe the inhibition to the sorption of component i caused by component j. A comparison of the competition coefficients (a_{ij} and a_{ji}) in the sorption isotherm equation shows that the uptake of the strongly sorbed Zn(II) was almost unaffected by the presence of Cd(II) ($a_{31} = 0.010$), while the inhibition exerted in the reverse situation was strong ($a_{13} = 4.442$). On the other hand, Ni(II) and Zn(II) ions significantly inhibited the sorption of one another onto RHA ($a_{23} = 3.28$ and $a_{32} = 2.99$). The sorption of Cd(II) and Ni(II) ions was almost unaffected by the presence of each other ($a_{12} = 0.01$ and $a_{21} = 0.01$). The competition coefficients seem to prove that the sorption of Zn(II) ions onto RHA was inhibited by the presence of Ni(II) ions, while the sorption of Ni(II) ions was inhibited mainly by the presence of Zn(II) ions. This tends to suggest that the surface sites of the RHA are heterogeneous, and some of the sites may be specific to certain metals.[25]

Three-dimensional (3-D) sorption isotherm surfaces are used to evaluate the performance of the binary metal ion sorption system.[26,27] This method has been extended to represent the desorption equilibria for ternary metal ion systems by a series of 3-D plots. The residual concentration of one of the metals is taken as a parameter in these plots. A 3-D diagram is plotted on the basis of the randomly generated data, and the experimental data are fitted to a smooth surface according to the SRS model. The adsorption isotherm surfaces of Zn(II) and Ni(II) for RHA, as shown in Figure 2, were created by using the multicomponent SRS model and smoothed and fitted to the experimental sorption data. Randomly selected initial concentrations of Cd(II) were chosen as parameters. When both Zn(II) and Ni(II) ions were present in the solution together and the effect of Cd(II) was ignored, some reduction of the Zn(II) uptake was observed with increasing Ni(II) concentration (Figure 2b). The uptake of Ni(II) ions also decreased with increasing equilibrium Zn(II) concentration. The inhibition effect of Zn(II) ions on the sorption of Ni(II) ions increased with an increase in the equilibrium Ni(II) concentration. Figure 3a−c shows the plots of unadsorbed Cd(II) and Zn(II) ion concentration in solution at equilibrium against the Cd(II), Zn(II), and total metal uptakes by the RHA. The initial concentration of Ni(II) ions was taken as a parameter. It is found that the uptake of Cd(II) ions by the RHA was moderately affected by the presence of Zn(II) ions compared to that of Ni(II) ions (Figure 3a). The predicted data points for the Cd(II) uptake using the multicomponent SRS model are least accurate followed by that of Zn(II) and Ni(II) in that order. The deviations of the predicted data from the experimental data for Zn(II) ions were much more pronounced in the 3-D adsorption isotherm plots (Figure 3b). Since the expected increase in the inhibitory effects caused by the presence of the other metal ions at increasing concentrations was not observed, the predicted equilibrium uptake for Zn(II) ions was higher than the experimental value. There is a marked difference between the shape of the two isotherm surfaces for the binary systems: Ni(II) + Zn(II) and Cd(II) + Zn(II), as illustrated in Figures 2c and 3c, respectively. Since the uptake of Ni(II) ions was severely affected by the increase in the concentration of Zn(II) ions and vice versa, the Ni(II) + Zn(II) sorption surfaces (Figure 2c) were curved convexly upward on the sides. On the other hand, the Zn(II) uptake was not affected much by the presence of Cd(II), and the Cd(II) + Zn(II) sorption surfaces (Figure 3c) were curved concavely downward.

4. Conclusion

The present study shows that rice husk ash (RHA) is an effective sorbent for the individual and competitive removal of Cd(II), Ni(II), and Zn(II) metal ions from aqueous solution. Freundlich and Redlich−Peterson isotherms show very good fit with the experimental sorption equilibrium data for single metal ions. In the ternary metal ion mixtures, the affinity of the RHA for Zn(II) ions was marginally higher than that for Ni(II) or Cd(II), for both the single and ternary metal ion systems under the same experimental conditions. The net interactive effect of Cd(II), Ni(II), and Zn(II) ions on the sorption of Cd(II) ions by RHA was found to be antagonistic. On the basis of Marquardt′s percent standard deviation (MPSD) error function, the simultaneous sorption phenomena of Cd(II), Ni(II), and Zn(II) ions on the RHA can be satisfactorily and adequately represented by the SRS model.

Nomenclature

a_{ij} = competition coefficients of component i by component j, dimensionless

a_R = constant of Redlich−Peterson isotherm, $dm^3 \cdot mg^{-1}$

C_0 = initial concentration of adsorbate in solution, $mg \cdot dm^{-3}$

$C_{0,i}$ = initial concentration of each component in solution, $mg \cdot dm^{-3}$

C_e = unadsorbed concentration of the single-component at equilibrium, $mg \cdot dm^{-3}$

$C_{e,i}$ = unadsorbed concentration of each component in the ternary mixture at equilibrium, $mg \cdot dm^{-3}$

K_i = individual extended Langmuir isotherm constant of each component, $dm^3 \cdot mg^{-1}$

K_F = monocomponent (noncompetitive) constant of Freundlich isotherm of the single component, $(mg \cdot g^{-1})(dm^3 \cdot mg^{-1})^{-1/n}$

$K_{F,i}$ = individual Freundlich isotherm constant of each component, $(mg \cdot g^{-1})(dm^3 \cdot mg^{-1})^{-1/n}$

K_L = constant of Langmuir isotherm, $dm^3 \cdot mg^{-1}$

$K_{L,i}$ = individual Langmuir isotherm constant of each component, $dm^3 \cdot mg^{-1}$

K_R = constant of the Redlich−Peterson isotherm, $dm^3 \cdot g^{-1}$

m = mass of adsorbent per liter of solution, $g \cdot dm^{-3}$

n_m = number of measurements

n_p = number of parameters

n = monocomponent (noncompetitive) Freundlich heterogeneity factor of the single component, dimensionless

n_i = individual Freundlich heterogeneity factor of each component, dimensionless

N = number of data points

MPSD = Marquardt′s percent standard deviation

q_e = equilibrium single-component solid phase concentration, $mg \cdot g^{-1}$

$q_{e,i}$ = equilibrium solid phase concentration of each component in ternary mixture, $mg \cdot g^{-1}$

$q_{e,cal}$ = calculated value of solid phase concentration of adsorbate at equilibrium, $mg \cdot g^{-1}$

$q_{e,exp}$ = experimental value of solid phase concentration of adsorbate at equilibrium, $mg \cdot g^{-1}$

q_m = maximum adsorption capacity of adsorbent, $mg \cdot g^{-1}$

q_{max} = constant in extended Langmuir isotherm, $mg \cdot g^{-1}$

Greek symbols

α_i = constant in SRS model for each component, dimensionless

β = constant of Redlich−Peterson isotherm ($0 < \beta < 1$)

β_i = constant in SRS model for each component, dimensionless

η_i = multicomponent (competitive) Langmuir adsorption constant of each component, dimensionless

Literature Cited

(1) Srivastava, V. C.; Mall, I. D.; Mishra, I. M. Antagonistic competitive equilibrium modeling for the adsorption of ternary metal ions mixtures onto bagasse fly ash. *Ind. Eng. Chem. Res.* **2008**, *47* (9), 3129–3137.

(2) Apak, R.; Guclu, K.; Turgut, M. H. Modeling of copper(II), cadmium(II), and lead(II) adsorption on red mud. *J. Colloid Interface Sci.* **1998**, *203*, 122–130.

(3) Bayat, B. Comparative study of adsorption properties of Turkish fly ashes II. The case of chromium(VI) and cadmium(II). *J. Hazard. Mater.* **2002**, *B95*, 275–290.

(4) Deliyanni, E. A.; Matis, K. A. Sorption of Cd ions onto akaganeite-type nanocrystals. *Sep. Purif. Technol.* **2005**, *45*, 96–102.

(5) Goksungur, Y.; Uren, S.; Guvenc, U. Biosorption of cadmium and lead ions by ethanol treated waste baker′s yeast biomass. *Bioresour. Technol.* **2005**, *96*, 103–109.

(6) Jain, C. K.; Ram, D. Adsorption of lead and zinc on bed sediments of the river kali. *Water Res.* **1997**, *31* (1), 154–162.

(7) Banat, F.; Al-Asheh, S.; Mohai, F. Batch zinc removal from aqueous solution using dried animal bones. *Sep. Purif. Technol.* **2000**, *21*, 155–164.

(8) Leyva-Ramos, R.; Bernal-Jacome, L. A.; Acosta-Rodriguez, I. Adsorption of cadmium(II) from aqueous solution on natural and oxidized corncob. *Sep. Purif. Technol.* **2005**, *45*, 41–49.

(9) Shawabkeh, R.; Al-Harahsheh, A.; Al-Otoom, A. Copper and zinc sorption by treated oil shale ash. *Sep. Purif. Technol.* **2004**, *40*, 251–257.

(10) Feng, Q.; Lin, Q.; Gong, F.; Sugita, S.; Shoya, M. Adsorption of lead and mercury by rice husk ash. *J. Colloid Interface Sci.* **2004**, *278*, 1–8.

(11) Srivastava, V. C.; Mall, I. D.; Mishra, I. M. Characterization of mesoporous rice husk ash (RHA) and adsorption kinetics of metal ions from aqueous solution onto RHA. *J. Hazard. Mater.* **2006**, *B134*, 257–267.

(12) Srivastava, V. C.; Mall, I. D.; Mishra, I. M. Adsorption thermodynamics and isosteric heat of adsorption of toxic metal ions onto bagasse fly ash (BFA) and rice husk ash (RHA). *Chem. Eng. J.* **2007**, *132*, 267–278.

(13) Bhattacharya, A. K.; Mandal, S. N.; Das, S. K. Adsorption of Zn(II) from aqueous solution by using different adsorbents. *Chem. Eng. J.* **2006**, *123*, 43–51.

(14) Mane, V.; Mall, I. D.; Srivastava, V. C. Kinetic and equilibrium isotherm studies for the adsorptive removal of Brilliant Green dye from aqueous solution by rice husk ash. *J. Environ. Manage.* **2006**, *84*, 390–400.

(15) Satyawali, Y.; Balakrishnan, M. Removal of color from biomethanated distillery spentwash by treatment with activated carbons. *Bioresour. Technol.* **2007**, *98*, 2629–2635.

(16) Redlich, O.; Peterson, D. L. A useful adsorption isotherm. *J. Phys. Chem.* **1959**, *63*, 1024–1026.

(17) Bellot, J. C.; Condoret, J. S. Modelling of liquid chromatography equilibrium. *Process Biochem.* **1993**, *28*, 365–376.

(18) Yang, R. T. *Gas separation by adsorption processes*; Butterworths: Boston, MA, 1987.

(19) Sheindorf, C.; Rebhum, M.; Sheintuch, M. A Freundlich-type multicomponent isotherm. *J. Colloid Interface Sci.* **1981**, *79*, 136–142.

(20) Srivastava, V. C.; Mall, I. D.; Mishra, I. M. Modelling individual and competitive adsorption of cadmium(II) and zinc(II) metal ions from aqueous solution onto bagasse fly ash. *Sep. Sci. Technol.* **2006**, *41*, 2685–2710.

(21) Srivastava, V. C.; Mall, I. D.; Mishra, I. M. Equilibrium modelling of single and binary adsorption of cadmium and nickel onto bagasse fly ash. *Chem. Eng. J.* **2006**, *117*, 79–91.

(22) Srivastava, V. C.; Mall, I. D.; Mishra, I. M. Removal of cadmium(II) and zinc(II) metal ions from binary aqueous solution by rice husk ash. *Colloid Surf. A: Physicochem. Eng. Aspect* **2008**, *312*, 172–184.

(23) Marquardt, D. W. An algorithm for least-squares estimation of nonlinear parameters. *J. Soc. Ind. Appl. Math.* **1963**, *11*, 431–441.

(24) Sag, Y.; Akcael, B.; Kutsal, T. Ternary biosorption equilibria of chromium(VI), copper(II), and cadmium(II) on *Rhizopus arrhizus*. *Sep. Sci. Technol.* **2002**, *37*, 279–308.

(25) Sag, Y.; Akcael, B.; Kutsal, T. Application of multicomponent adsorptionmodels to the biosorption of Cr(II), Cu(II), and Cd(II) ions on rhizopus arrhizus from ternary metal mixtures. *Chem. Eng. Commun.* **2003**, *190*, 797–812.

(26) de Carvalho, R. P.; Chong, K. H.; Volesky, B. Evaluation of the Cd, Cu and Zn biosorption in two-metal systems using algal biosorbent. *Biotechnol. Prog.* **1995**, *11*, 39–44.

(27) Chong, K. H.; Volesky, B. Metal biosorption equilibria in a ternary system. *Biotechnol. Bioengg.* **1996**, *49*, 629–638.

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