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Modelling Individual and Competitive Adsorption of Cadmium(II) and Zinc(II) Metal Ions from Aqueous Solution onto Bagasse Fly Ash

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Abstract: The present study deals with the competitive adsorption of cadmium (Cd(II)) and zinc (Zn(II)) ions onto bagasse fly ash (BFA) from binary systems. BFA is a waste obtained from the bagasse-fired boilers of sugar mills. The initial $\mathrm{pH} \approx 6.0$ is found to be the optimum for the individual removal of Cd(II) and Zn(II) ions by BFA. The equilibrium adsorption data were obtained at different initial concentrations ($C_0 = 10-100\ \mathrm{mg/l}$), 5 h contact time, 30°C temperature, BFA dosage of 10 mg/l at $pH_0 = 6$. The Redlich–Peterson (R–P) and the Freundlich models represent the single ion equilibrium adsorption data better than the Langmuir model. The adsorption capacities in the binary-metal mixtures are in the order $\mathrm{Zn(II)} > \mathrm{Cd(II)}$ and is in agreement with the single-component adsorption data. The equilibrium metal removal decreases with increasing concentrations of the other metal ion and the combined action of Cd(II) and Zn(II) ions on BFA is found to be antagonistic. Equilibrium isotherms for the binary adsorption of Cd(II) and Zn(II) ions on BFA have been analyzed by non-modified Langmuir, modified Langmuir, extended-Langmuir, Sheindorf–Rebuhn–Sheintuch (SRS), non-modified R–P and modified R–P adsorption models. The isotherm model fitting has been

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done by minimizing the Marquardt's percent standard deviation (MPSD) error function using MS Excel. The SRS model satisfactory fits for most of the adsorption equilibrium data of Cd(II) and Zn(II) ions onto BFA.

Keywords: Binary adsorption, bagasse fly ash (BFA), simultaneous metal removal, multi-component isotherms, cadmium(II), zinc(II)

INTRODUCTION

Heavy metals are considered as hazardous pollutants due to their toxicity even at low concentration, and non-biodegradable properties. The transportation and bioavailability of heavy metals in the aquatic system is affected greatly by their binding to surfaces of solid phases and complexion with the ligands in the water. Heavy metals contaminants exist in aqueous waste streams of many industries like metallurgical/metal manufacturing and electroplating, chemical manufacturers, printing industry, dye and paint industry, paper industry, textile industry, refinery and petrochemical industry, leather products industry, fertilizer industry, pesticides industry, etc. Increasing presence of heavy metals in waste stream and ground water has become one of the most serious environmental pollution problem due to their acute toxicity and non-biodegradable nature. These metals have cumulative effects and tend to accumulate in the living organisms causing various diseases and disorders. Cadmium [Cd(II)] is non-essential and non-biodegradable, and slowly accumulates in the body usually from foods. The body slowly releases adsorbed Cd(II) which has a biological half-life of more than 10 years. As a consequence, the Cd(II) content of the kidney increases throughout life from zero to about 20 mg in a middle-aged non-smoker and more than twice as much in an adult smoker. Ingested Cd(ll) is transported to other organs by the blood, where it is bound by glutathione and haemoglobin in the red blood cells (1). Cadmium accumulation in the kidneys causes its malfunction at overdoses spilling proteins in the urine and disrupting protein metabolism (2). Consumption of rice containing high concentrations of cadmium led to a surge in the Itai-Itai disease in Japan in 1955 (3). In humans Zinc [Zn(II)] occurs in over 20 metalloenzymes, including several that are involved in nucleic acid metabolism. Its excess ingestion results in acute gastrointestinal disturbances accompanied with nausea. Instances of zinc toxicity from ingestion of fruit juices that were stored in galvanized (zinc plated) steel containers have been reported (4). Due to toxicity of metals, the Ministry of Environment and Forests (MOEF), Government of India has set Minimal National Standards (MINAS) of 0.2 and 5.0 mg/l, respectively, for Cd(II) and Zn(II) for safe discharge of the effluents containing these metal ions into surface waters (5). The main techniques utilized to remove heavy metal ions from aqueous streams include ion-exchange, reverse-osmosis, precipitation, and adsorption. Adsorption as a wastewater treatment process has aroused considerable interest during recent years. The use of a commercially available adsorbent, activated carbon is limited, especially in developing countries, because of its relatively high cost and the difficulties associated with its regeneration. As a result, unconventional adsorbents like bagasse fly ash (BFA), 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 (6–13).

The sugar industry is one of the most important agri-based industries in India, South America, and the Caribbean countries. BFA, a waste collected from the particulate collection equipment attached upstream to the stacks of bagasse-fired boilers, causes disposal problems. It is mainly used for land filling, and partly used as a filler in building materials and paper and wood boards. BFA has good adsorptive properties and has been used for the removal of COD and color from sugar mill (14) and paper mill effluents (15). Various researchers have utilized it for the adsorptive removal of phenolic compounds (16), and dyes (17–19). 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 can contain several metals, it is necessary to study the simultaneous sorption of two or more metals and also to quantify the interference of one metal with the sorption of the other. Thus the studies on equilibrium and kinetics of adsorption of heavy metals from binary and ternary systems are very important. Various single component equilibrium adsorption isotherm equations have been extended and modified for use in binary and multi-component systems. No information is available in literature for the simultaneous removal of Cd(II) and Zn(II) ions by BFA.

The present paper aims to

(i) study the feasibility of using BFA as an adsorbent for the individual and simultaneous removal of Cd(II) and Zn(II) metal ions from aqueous solutions,
(ii) study the effect of initial pH (pH_0),
(iii) determine the applicability of non-competitive adsorption isotherm models (i.e., Freundlich, Langmuir, and Redlich–Peterson (R–P)) based on the regression analysis for single component,
(iv) gather experimental data on adsorption equilibrium for the binary system containing Cd(II) and Zn(II) ions; and
(v) examine the applicability of the multicomponent adsorption isotherm equations to the competitive adsorption equilibria of the metals in binary system.

THEORY

Monocomponent Isotherm Equations

To optimize the design of an adsorption system for the adsorption of adsorbates, it is important to establish the most appropriate correlation for the equilibrium curves. Various isotherm equations like those of Freundlich, Langmuir, and Redlich–Peterson (R–P) have been used to describe the equilibrium characteristics of adsorption.

The Freundlich isotherm (20) is derived by assuming a heterogeneous surface with a non-uniform distribution of heat of adsorption over the surface. Whereas in the Langmuir theory (21), the basic assumption is that the sorption takes place at specific homogeneous sites within the adsorbent.

The R–P isotherm (22) can be described as follows:

$$q_e = \frac{K_R C_e}{1 + a_R C_e^{\beta}} \tag{1}$$

where K_R is R–P isotherm constant (l/g), a_R is R–P isotherm constant (l/mg) and β is the exponent which lies between 0 and 1, C_e is the equilibrium liquid phase concentration (mg/l).

For high concentrations, Eq. (1) reduces to Freundlich isotherm

$$q_e = K_F C_e^{1/n} \quad \text{or} \quad \ln q_e = \ln K_F + n \ln C_e \tag{2}$$

where, $K_F = K_R/a_R$ is the Freundlich constant (l/mg), and $(1/\mathrm{n}) = (1 - \beta)$ is the heterogeneity factor.

For $\beta = 1$, Eq. (1) reduces to Langmuir equation, i.e.

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad \text{or} \quad \frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \tag{3}$$

where, K_L $(= a_R)$ is the Langmuir adsorption constant (l/mg) related to the energy of adsorption and q_m $(= K_R/a_R)$ signifies adsorption capacity (mg/g).

For $\beta = 0$, Eq. (1) reduces to Henry's equation, i.e.

$$q_e = \frac{K_R C_e}{1 + a_R} \tag{4}$$

The R–P isotherm incorporates three parameters and can be applied either in homogenous or heterogeneous systems. Eq. (1) can be converted to a linear form by taking logarithms of both the sides as

$$\ln\left(K_R \frac{C_e}{q_e} - 1\right) = \ln a_R + \beta \ln C_e \tag{5}$$

A minimization procedure has been adopted to solve Eq. (5) by maximizing the correlation coefficient between the predicted values of q_e from Eq. (5) and the experimental data using the solver add-in function of the MS excel.

Multicomponent Isotherm Equations

Non-Modified Competitive Langmuir Model

The extension of the basic Langmuir model for component *i* in a *N*-component system to competitive adsorption can be formulated as follows:

$$q_{e,i} = \frac{q_{m,i} K_{L,i} C_{e,i}}{1 + \sum_{j=1}^{N} K_{L,j} C_{e,j}} \tag{6}$$

where, $q_{m,i}$ and $K_{L,i}$ are derived from the corresponding individual Langmuir isotherm equations.

Modified Competitive Langmuir Isotherm

Individual adsorption constants may not define exactly the multi-component adsorption behavior of metal ion mixtures. For that reason, better accuracy may be achieved by using modified isotherms related to the individual isotherm parameters and the correction factors. An interaction term, $\eta_{L,i}$, which is a characteristic of each species and depends on the concentrations of the other components, has been added in the competitive Langmuir model (23). The modified competitive Langmuir isotherm is given as

$$q_{e,i} = \frac{q_{m,i} K_{L,i} (C_{e,i}/\eta_{L,i})}{1 + \sum_{j=1}^{N} K_{L,j} (C_{e,j}/\eta_{L,j})} \tag{7}$$

where, $q_{m,i}$ and $K_{L,i}$ are derived from the corresponding individual Langmuir isotherm equations, and $\eta_{L,i}$ are estimated from competitive adsorption data. For binary mixtures, this equation can be rewritten as for the first and the second component, respectively, and the two equations can be solved simultaneously to obtain the multicomponent Langmuir adsorption constants of the first and the second components, respectively.

Extended Langmuir Isotherm

Assuming that the surface sites are uniform, and that all the adsorbate molecules (ions) in the solution compete for the same surface sites, (24) extended the Langmuir equation for multicomponent systems as

$$q_{e,i} = \frac{q_{\max} K_i C_{e,i}}{1 + \sum_{j=1}^{N} K_j C_{e,j}} \tag{8}$$

Sheindorf–Rebuhn–Sheintuch (SRS) Model

Sheindorf et al. (25) derived a Freundlich-type multi-component adsorption isotherm known as the Sheindorf–Rebuhn–Sheintuch (SRS) equation, to represent the experimental data. A general SRS equation for the adsorption isotherm for component i in a N-component system is given as:

$$q_{e,i} = K_{F,i} C_{e,i} \left(\sum_{j=1}^{N} a_{ij} C_{e,j} \right)^{n_i - 1} \tag{9}$$

The pre-exponential coefficient $K_{F,i}$ and the exponent n_i is determined from the mono-component systems. The competition coefficients a_{ij} describe the inhibition to the adsorption of component i by component j, and can be determined from the thermodynamic data, or more likely, from the experimental data of multicomponent systems. The SRS equation assumes that

(i) each component individually obeys the Freundlich isotherm;
(ii) that for each component in a multicomponent adsorption system, there exists an exponential distribution of site adsorption energies.

$$N_i(Q) = \alpha_i \exp(-\beta_i Q/RT) \tag{10}$$

where, α_i and β_i are constants; and
(iii) the coverage by each adsorbate molecule (or ion) at each energy level Q is given by the multicomponent Langmuir isotherm equation:

$$\theta_i(Q) = \frac{K_i C_{e,i}}{1 + \sum_{j=1}^{N} K_j C_{e,j}} \tag{11}$$

where,

$$K_j = K_{0j} \exp\left(\frac{Q}{RT} \right) \tag{12}$$

Integration of $N_i(Q)\theta_i\ (Q)$ over energy level in the range of $-\infty$ to $+\infty$ yields Eq. (11) and the competition coefficients are defined as $a_{ij} = K_{0j}/K_{0i}$ and thus $a_{ji} = 1/a_{ij}$. The SRS equation has been successfully applied to a multicomponent equilibrium adsorption of different types of contaminants (25–28).

Non-Modified Competitive Redlich–Peterson Model

The competitive non-modified R–P model related to the individual isotherm parameters only is given as follows:

$$q_{e,i} = \frac{K_{R,i} C_{e,i}}{1 + \sum_{j=1}^{N} a_{R,j} C_{e,j}^{\beta,j}} \tag{13}$$

where, $K_{R,i}$, $a_{R,i}$ and β_i are the R–P parameters derived from the corresponding individual R–P isotherm equations

Modified Competitive Redlich–Peterson Model

The competitive non-modified R–P model is modified to the following modified competitive R–P Model to take the characteristic of each species into account.

$$q_{e,i} = \frac{K_{R,i}(C_{e,i}/\eta_{R,i})}{1 + \sum_{j=1}^{N} a_{R,j}(C_{e,j}/\eta_{R,j})^{\beta,j}} \tag{14}$$

where, $\eta_{R,i}$ are estimated from competitive adsorption data.

Determination of Isotherm Parameters

The isotherm parameters of all the multi-component models were found by using the MS Excel 2002 for Windows by minimizing Marquardt's percent standard deviation (MPSD) (29). MPSD has been used by a number of researchers in the field (17, 18, 30) to test the adequacy and accuracy of various isotherm model fit with the experimental data. It has some similarity to the geometric mean error distribution, but modified by incorporating the number of degrees of freedom. This error function is given as

$$MPSD = 100\sqrt{\frac{1}{n_m - n_p}\sum_{i=1}^{n}\left(\frac{q_{e,i,\text{exp}} - q_{e,i,\text{cal}}}{q_{e,i,\text{exp}}}\right)^2} \tag{15}$$

In the above equation, the subscript "exp" and "calc" shows the experimental and calculated values and n_m the number of measurements and n_p the number of parameters in the model.

The $q_{e,i}$, individual adsorption yield ($Ad_i\%$) and total adsorption yields ($Ad_{Tot}\%$) can be calculated by using the following expressions:

$$q_{e,i} = (C_{0,i} - C_{e,i})V/w, \text{(mg of adsorbate/g of adsorbent)} \tag{16}$$

$$Ad_i\% = 100(C_{0,i} - C_{e,i})/C_{0,i} \tag{17}$$

$$Ad_{Tot}\% = 100\sum(C_{0,i} - C_{e,i})/\sum C_{0,i} \tag{18}$$

where, V is the volume of the adsorbate containing solution (l) and w is the mass of the adsorbent (g).

EXPERIMENTAL

BFA

BFA was used as obtained from a nearby sugar mill (Deoband Sugar Mill, U.P., India) as such without any pretreatment for the removal of Cd(II) and

Zn(II) from synthetic aqueous solutions in a batch treatment process. Detailed physico-chemical characteristics of the BFA have already been presented elsewhere (15, 16).

Chemicals

All the chemicals used in the study were of analytical reagent (AR) grade. Cadmium sulphate octahydrate ($3CdSO_4 \cdot 8H_2O$), Zinc sulphate heptahydrate ($ZnSO_4 \cdot 7H_2O$), NaOH and HCl were obtained from S.D. fine Chemicals, Mumbai. Stock solutions of Cd(II) and Zn(II) were made by dissolving the exact amount of $CdSO_4 \cdot 8H_2O$ and $ZnSO_4 \cdot 7H_2O$ in distilled water, respectively. The range of concentration of both components prepared from the stock solution varied between 10 to 100 mg/l. These test solutions were prepared by diluting 1 g/l of stock solution of Cd(II) and Zn(II).

Batch Adsorption Studies

For each experimental run, 100 ml aqueous solution of known concentration of Cd(II), Zn(II) or binary mixture of these components was taken in 250 ml conical flask containing 1 g of BFA. 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. The initial pH (pH_0) of the adsorbate solution was adjusted using 1 N (36.5 g/l) HCI or 1 N (40 g/l) NaOH aqueous solution without any further adjustment during the sorption process. The samples were withdrawn from the flasks after 5 h, centrifuged using Research Centrifuge (Remi Instruments, Mumbai) at 5000 rpm for 5 min and then the supernatant liquid was analyzed for residual concentration of metal ions using atomic adsorption spectrophotometer (GBC Avanta Instrument).

Effect of Initial pH (pH_0)

The effect of pH_0 on the sorption was studied by adjusting the pH_0 in the range of 2–10. In these experiments, the BFA loading was kept at 10 g/l of solution containing 30 mg/l each of Cd(II) and Zn(II) at 30°C. At pH_0 6.0, the Cd(II) and Zn(II) uptake by BFA was found to be 2.38 and 2.60 mg/g at 5 h, 2.41 and 2.62 mg/g at 12 h, and 2.42 and 2.64 at 24 h of contact time (t), respectively. Since the difference in the metals uptake at 5 h and 24 h was less than 2% of that at 24 h, therefore, after a 5 h contact time, a steady state approximation was assumed and a quasi-equilibrium situation was accepted. Accordingly, all the batch experiments were conducted with a contact time of 5 h at a constant shaking rate of 150 rpm.

Adsorption Isotherm Experiments

For single metal-BFA systems, the initial metal ion concentration was varied from 10 to 100 mg/l. In binary metal ion mixture-BFA systems, for each initial concentration of the Cd(II) solution: viz., 10, 20, 30, 50, and 100 mg/l, the Zn(II) concentration was varied in the range of 10–100 mg/l (viz., 10, 20, 30, 50, and 100 mg/l. In all cases, the pH_0 of the solution was maintained at 6.0. This pH_0 was found to be the optimum on the basis of batch tests conducted to determine the effect of pH_0 on the adsorption capacity of BFA for metal ions.

Analysis of Cadmium(II) and Zinc(II)

Cd(II) and Zn(II) in the sample was determined by a flame atomic absorption spectrophotometer (GBC Avanta, Australia) at the wavelength of 228.8 nm and 213.9 nm, for Cd(II) and Zn(II) respectively, by using air–acetylene flame. Metal ion concentrations were determined by reference to appropriate standard metal ion solutions.

RESULTS AND DISCUSSION

Effect of Initial pH (pH_0)

The pH of the adsorbate solutions has been identified as the most important parameter governing sorption on different adsorbents (31). This is partly due to the fact that hydrogen ions themselves are strong competing sorbates and partly that the solution pH influences the chemical speciation of metal ions. It is known that metal species [M(II) = Cd(II), Zn(II)] are present in deionized water in the forms of M^{2+}, $M(OH)^+$, $M(OH)_2^0$, $M(OH)_{2(S)}$, etc. (32). At pH $\approx$ 5.0, the solubility, $C_{T,M}$, of the $M(OH)_{2(S)}$ is high, and therefore, the M^{2+} is the main species in the solution. With the increase of the pH value, the $C_{T,M}$ of $M(OH)_{2(S)}$ decreases and at pH $\approx$ 10.0, the $C_{T,M}$ of $M(OH)_{2(S)}$ is very small. At this time, the main species in the solution is $M(OH)_{2(S)}$. It is obvious that the adsorption of M(II) must be higher at alkaline range. However, in the alkaline range, the metal precipitation plays the main role in the removal of the M(II) ions attributed to the formation of precipitate of $M(OH)_{2(S)}$ as discussed above. To avoid precipitation of the metal ions, all the experiments were conducted at a maximum pH_0 of 6.0. The effect of pH_0 on the removal of individual Cd(II) and Zn(II) ions by BFA is shown in Fig. 1. The removal of metal ions was found to increase when the pH_0 was increased from 3.0 to 6.0. The maximum uptake of metal ions was obtained at about pH_0 6.0 and, thereafter, the removal was observed to be nearly constant. The oxides of alumina, calcium, and silica

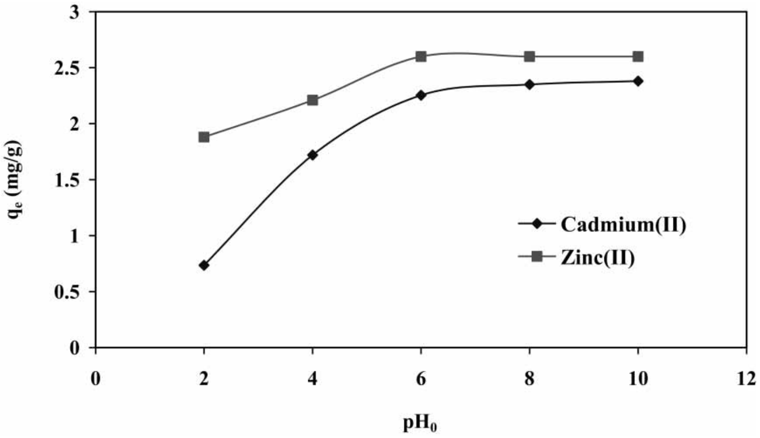

Figure 1. Effect of pH_0 on the removal of cadmium(II) and zinc(II) ions for single adsorbate aqueous solution by BFA. $T = 30°C$, $t=5$ h, $C_0 = 30$ mg/l, BFA dosage = 10 g/l.

present in the BFA develop a charge in contact with water. Except silica, all other oxides possess a positive charge for the pH range of interest because zero point charge (pH_{ZPC}) of SiO_2, Fe_2O_3, Al_2O_3 and CaO are 2.2, 6.7, 8.5, and 11.0, respectively. A positive charge develops on the surface of the oxides of BFA in an acidic medium due to aqua complex formation of the oxides present as follows:

$$-MO + H - OH \xrightarrow{H^+} M - OH^{2+} + OH^-$$

Cd(II) and Zn(II) ion adsorption at low pH_0 ($pH_0 \leq 6.0$) is lesser in comparison to that at higher pH_0 (≥ 6.0). This is due to the fact that the surface charge developed at low pH_0 is not suitable for the adsorption of these metal ions. For pH_0 below 6, a significant electrostatic repulsion exists between the positively charged surface of the BFA and the cationic metal ions. Besides this, a higher concentration of H^+ in the solution competes with Cd(II) and Zn(II) for the adsorption sites, resulting in the reduced uptake of metal ions. As the pH_0 of the system increases, the number of positively charged sites decreases and the number of negatively charged sites increases on the surface of BFA as shown below:

$$MOH + OH^- \longrightarrow -MO^- + H_2O$$
$$MO^- + Zn \longrightarrow -MO - O - Zn$$

A negatively charged surface site on the BFA favors the adsorption of cationic metal ions due to electrostatic attraction. Similar theories have been proposed by Viraraghavan and Rao (33) and Mathialagan and Viraraghavan

(34) for metal adsorption on fly ash which were also made up of various oxides. Similar results have been reported by other researchers, e.g. for the uptake of Zn, Cd, and Cu onto activated carbon (35), for the uptake of Zn, Cd, and Cu onto a selected mixture of mosses (36). It is also clear that the amount of adsorbed zinc is larger than that of cadmium. This may be due to the smaller size of the zinc atom compared with that of cadmium.

Single and Binary Adsorption of Cadmium(II) and Zinc(II) Ions

The equilibrium uptakes and the adsorption yields obtained for single component (Cd(II) and Zn(II)) solution at pH_0 6.0 are shown in Table 1. As seen from this table, the adsorption capacity of BFA for Zn(II) is generally greater than that of the Cd(II). Also, increasing the initial metal concentration up to 100 mg/l increases the equilibrium uptake and decreases the adsorption yield of both the components. When the initial ion concentration increases from 10 mg/l to 100 mg/l, the loading capacity of BFA increased from 0.89 mg/g to 5.18 mg/g for Cd(II) and from 0.96 mg/g to 6.27 mg/g for Zn(II). The initial concentration provides the necessary driving force to overcome the resistances to the mass transfer of Cd(II) and Zn(II) ions between the aqueous and the solid phases. The increase in initial concentration also enhances the interaction between the metal ions in the aqueous phase and the BFA. Therefore, an increase in initial concentration of metal ions enhances the adsorption uptake of the Cd(II) and Zn(II) ions.

The simultaneous adsorption of Cd(II) and Zn(II) ions from binary mixtures was also investigated at pH_0 6.0. In the first stage of adsorption studies, while initial Cd(II) concentration was changed from 0 to 100 mg/l, at each initial Zn(II) ion concentration of 0, 10, 20, 30, 50, 100 mg/l. It is seen from Table 1 that the equilibrium Cd(II) uptake increases with increasing initial Cd(II) concentration up to 100 mg/l at all Zn(II) ion concentrations. The equilibrium uptake of Cd(II) decreases regularly with increasing Zn(II) ion concentration. A similar trend is obtained for the uptake of Zn(II) ion in the absence and presence of Cd(II) ion. In general, the increase in concentration of ion metal ion not only decreases the individual adsorption yields of other metal ions, but also decreases the total adsorption yields for each experimental run. At 100 mg/l initial Cd(II) concentration, in the absence of Zn(II) ions and in the presence of 100 mg/l Zn(II) ion concentration, adsorbed Cd(II) quantities at equilibrium are found to be 5.18 and 3.70 mg/g, respectively. Similarly, with no Cd(II) present in the solution, equilibrium Zn(II) uptake is found as 6.27 mg/g at 100 mg/l initial Zn(II) ion concentration. When the Cd(II) concentration is kept at 100 mg/l at the same initial Zn(II) ion concentration, the equilibrium Zn(II) uptake decreases to 3.87 mg/g.

In general, a mixture of different adsorbates may exhibit three possible types of behavior: synergism (the effect of the mixture is greater than that

Table 1. Comparison of individual and total adsorption equilibrium uptakes and yields found at different cadmium(II) concentrations in the absence and presence of increasing concentrations of zinc(II) ions onto bagasse fly ash

$C_{0,Cd}$	$C_{0,Zn}$	$C_{e,Cd}$	$C_{e,Zn}$	$q_{e,Cd}$	$q_{e,Zn}$	$Ad_{Cd}\%$	$Ad_{Zn}\%$	$Ad_{Tot}\%$
0	0	0	0	0	0	0	0	0.00
10	0	1.10	0	0.89	0	89.00	0	89.00
20	0	3.98	0	1.60	0	80.10	0	80.10
30	0	7.46	0	2.25	0	75.13	0	75.13
50	0	17.10	0	3.29	0	65.80	0	65.80
100	0	48.24	0	5.18	0	51.76	0	51.76
0	10	0	0.40	0	0.96	0	96.00	96.00
10	10	2.00	1.37	0.80	0.86	80.00	86.29	83.14
20	10	5.90	2.60	1.41	0.74	70.50	74.00	71.67
30	10	9.90	4.00	2.01	0.60	67.00	60.00	65.25
50	10	21.50	4.38	2.85	0.56	57.00	56.22	56.87
100	10	49.60	5.13	5.04	0.49	50.40	48.71	50.25
0	20	0	1.80	0	1.82	0	91.00	91.00
10	20	3.00	4.40	0.70	1.56	70.00	78.00	75.33
20	20	7.90	5.98	1.21	1.40	60.50	70.10	65.30
30	20	13.60	8.60	1.64	1.14	54.67	57.00	55.60
50	20	24.00	9.20	2.60	1.08	52.00	54.00	52.57
100	20	52.90	10.88	4.71	0.91	47.10	45.61	46.85
0	30	0	4.00	0	2.60	0	86.67	86.67
10	30	4.00	8.00	0.60	2.20	60.00	73.33	70.00
20	30	9.07	10.50	1.09	1.95	54.64	65.00	60.86
30	30	14.63	13.25	1.54	1.68	51.24	55.84	53.54
50	30	26.10	14.20	2.39	1.58	47.80	52.67	49.63
100	30	54.90	17.30	4.51	1.27	45.10	42.33	44.46
0	50	0	11.00	0	3.90	0	78.00	78.00
10	50	4.67	16.00	0.53	3.40	53.26	68.00	65.54
20	50	10.09	19.33	0.99	3.07	49.56	61.34	57.97
30	50	15.77	23.29	1.42	2.67	47.44	53.42	51.18
50	50	28.00	25.30	2.20	2.47	44.00	49.40	46.70
100	50	59.80	29.83	4.02	2.02	40.20	40.34	40.25
0	100	0	37.30	0	6.27	0	62.70	62.70
10	100	4.98	43.70	0.50	5.63	50.21	56.30	55.75
20	100	10.82	45.90	0.92	5.41	45.89	54.10	52.73
30	100	16.83	48.10	1.32	5.19	43.91	51.90	50.06
50	100	29.80	54.80	2.02	4.52	40.40	45.20	43.60
100	100	63.00	61.30	3.70	3.87	37.00	38.70	37.85

of each of the individual adsorbates in the mixture), antagonism (the effect of the mixture is less than that of each of the individual adsorbates in the mixture), and non-interaction (the mixture has no effect on the adsorption of each of the adsorbates in the mixture). The combined effect of the two components viz. Cd(II) and Zn(II) seem to be antagonistic. To analyze the antagonistic adsorption interaction of the two metal ions, the adsorption yields of single- and binary component systems were also compared. For instance, using Table 1, it was expected that the total adsorption yield must be equal to 57.23% for the total metal concentration of 200 mg/l containing equal (100 mg/l) concentration of Cd(II) and Zn(II) in the mixture [$Ad_{Tot}\% = 57.23 = 100 \times$ [(51.76 mg/l Cd(II) + 62.70 mg/l Zn(II) ion)/ 200 mg/l initial total concentration], but from Table 1, the experimental total adsorption yield was 37.85% for total 200 mg/l Cd(II) and Zn(II) ion mixture consisting of 100 mg/l each of Cd(II) and Zn(II) ion together [$Ad_{Tot}\% = 37.85 = 100 \times$ [(37.00 mg/l Cd(II) + 38.70 mg/l Zn(II) ion)/ 200 mg/l initial total concentration]. As a result, the binary solution exhibited inhibitory (antagonistic) effects resulting in a lower sorption yield.

The experimental equilibrium sorption data obtained for the single component and the binary systems indicate that the adsorption capacity of BFA for Cd(II) is, in general, less than that of Zn(II). There are possible interaction effects between different species in solution and in particular potential interactions on the surface depending on the adsorption mechanism. Factors that affect the adsorption preference of an adsorbent for different kinds of adsorbates may be related to the characteristics of the binding sites (e.g. functional groups, structure, surface properties, etc.), the properties of the adsorbates (e.g. concentration, ionic size, ionic weight, ionic charge, molecular structure, ionic nature, or standard redox potential, etc.) and the solution chemistry (e.g. pH, ionic strength, etc.). To deduce a common denominator from the physical and chemical properties of Cd(II) and Zn(II) ions to identify how these properties interact and affect the selective sorption of an adsorbate seems to be difficult at the moment. However, it appears that the two metal ions share the binding sites on the surface of BFA.

Single-Component Adsorption Isotherm

To optimize the design of an adsorption system for the adsorption of adsorbates, it is important to establish the most appropriate isotherm model. Various isotherm equations like those of Freundlich, Langmuir, and R–P have been used to describe the mono-component equilibrium characteristics of adsorption of Cd(II) and Zn(II) ions by BFA. The experimental equilibrium adsorption data were obtained by varying the concentrations of Cd(II) or Zn(II) ions with a fixed dosage of BFA (10 g/l).

The Langmuir, Freundlich, and R–P adsorption isotherms for Cd(II) and Zn(II) at pH_0 6.0 are shown in Figs. 2 to 4, respectively. The individual adsorption parameters for each metal ion obtained from the fitting of different isotherm models are listed in Table 2 with the linear regression coefficients, R^2. The R^2 values are closer to unity for the R–P and the Freundlich models than that for the Langmuir model. Therefore, the equilibrium

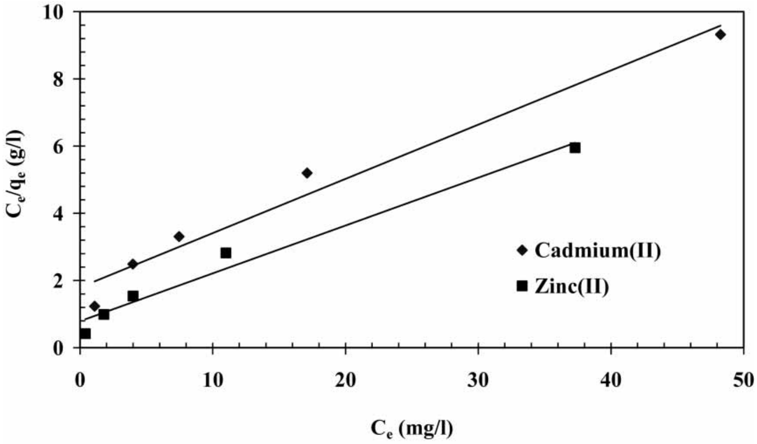

Figure 2. Mono-component Langmuir isotherm plots for the removal of cadmium(II) and zinc(II) ions by BFA. $pH_0 = 6.0$, T = 30°C, $t = 5$ h, $C_0 = 10-100$ mg/l, BFA dosage = 10 g/l.

adsorption data of Cd(II) and Zn(II) ion adsorption on BFA can be represented more appropriately by the R–P and the Freundlich models in the studied concentration range. At lower concentrations, the Langmuir isotherm does not represent the equilibrium sorption. The single-component Langmuir constant, q_m, is the monolayer saturation at equilibrium. The

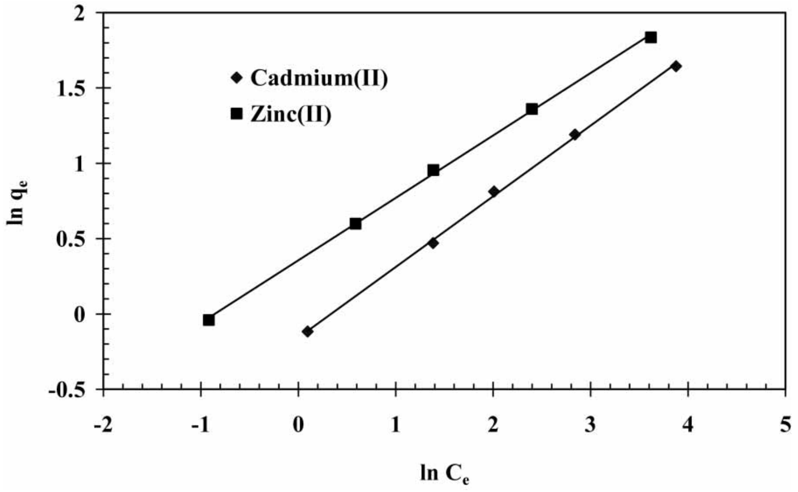

Figure 3. Mono-component Freundlich isotherm plots for the removal of cadmium(II) and zinc(II) ions by BFA. $pH_0 = 6.0$, T = 30°C, $t = 5$ h, $C_0 = 10-100$ mg/l, BFA dosage = 10 g/l.

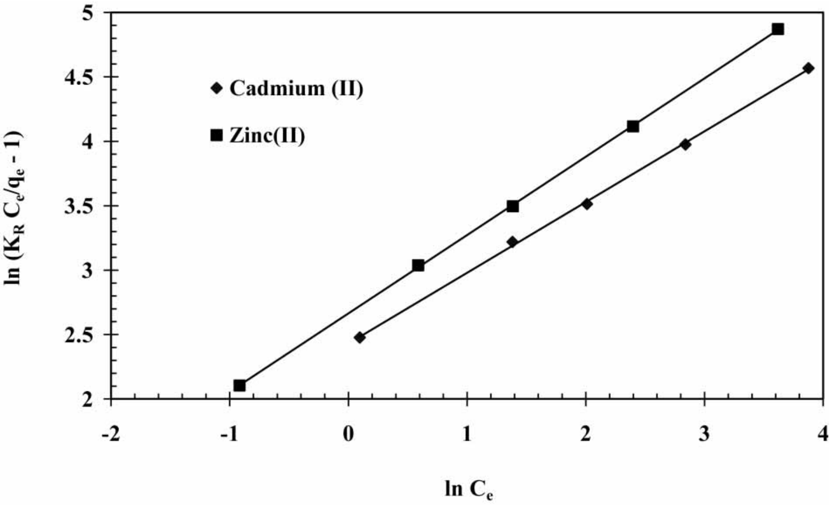

Figure 4. Mono-component Redlich–Peterson isotherm plots for the removal of cadmium(II) and zinc(II) ions by BFA. $pH_0 = 6.0$, T = 30°C, $t = 5$ h, $C_0 = 10–100$ mg/l, BFA dosage = 10 g/l.

other single-component Langmuir constant, K_L, corresponds to the concentration at which the amount of a Cd(II) or a Zn(II) ion bound to the BFA is equal to $q_m/2$. This indicates the affinity of the Cd(II) or Zn(II) ions to bind with BFA. A high K_L value indicates a higher affinity. The data in Table 2 also indicate that the amount of Zn(II) ions per unit weight of BFA for the complete monolayer surface coverage was higher than that of Cd(II).

Table 2. Isotherm parameters values for the removal of cadmium(II) and zinc(II) by bagasse fly ash

Langmuir constants				
Adsorbate	K_L (l/mg)		q_m (mg/g)	R^2
Cadmium(II)	0.09		6.19	0.99
Zinc(II)	0.18		7.03	0.99
Freundlich constants				
Adsorbate	K_F ((mg/g)/(mg/l)$^{1/n}$)		n	R^2
Cadmium(II)	0.85		0.47	1
Zinc(II)	1.43		0.42	1
Redlich–Peterson constants				
Adsorbate	K_R (l/g)	a_R (l/mg)	β	R^2
Cadmium(II)	10.44	11.37	0.55	1
Zinc(II)	22.09	14.36	0.61	1

A large value of K_L also implies the strong bonding of Zn(II) ions to BFA. K_F and n, the single-component Freundlich constants, indicate the adsorption capacity and adsorption intensity, respectively. The higher the value of n, the higher will be the affinity and the heterogeneity of the adsorbent sites. It is found from Table 2 that the BFA shows greater heterogeneity for Cd(II) than that for Zn(II) ions. Since $n < 1$; both the Cd(II) and Zn(II) ions are favorably adsorbed by BFA at pH_0 6.0. The magnitude of K_F also showed the higher uptake of Zn(II) than that of Cd(II) ions by BFA at pH_0 6.0.

It is noted that Redlich–Peterson constant, β normally lies between 0 and 1, indicating a favorable adsorption. The values of the Freundlich and Langmuir constants have been reported in the literature, under different environmental conditions. The comparative assessment of these values with the values obtained in the present work is shown in Table 3. It may be seen that the isotherm parameters differ widely in their values for different adsorbents. Hence one should be cautious while using these values in the design of adsorption systems. A comparison of q_m values with the one obtained in the present study shows that the BFA exhibits a reasonable capacity for Cd(II) and Zn(II) adsorption from aqueous solutions. The comparison of the experimental and predicted equilibrium uptakes (q_e) evaluated from the single-component Langmuir, Freundlich, and Redlich–Peterson models for the individual adsorption of Cd(II) and Zn(II) onto BFA at pH_0 6.0 are presented in Table 4 along with the MPSD values. In view of the lower MPSD values, the R–P and Freundlich models show better fit to the experimental adsorption data than the Langmuir model.

Multi-Component Adsorption Models

The simultaneous adsorption data of Cd(II) and Zn(II) on the BFA have been fitted to the multi-component isotherm models, viz., non-modified, modified, and extended Langmuir models; the SRS model; non-modified and modified R–P models. The parametric values of all the multicomponent adsorption models are given in Table 5. The MPSD values between the experimental and calculated q_e values for the entire data set of Cd(II) and Zn(II) are also given in Table 5. The comparisons of the experimental and calculated q_e values of Cd(II) and Zn(II) ion in mixtures are also presented in the parity plots Figs. 5 and 6. Except for non-modified Langmuir and R–P models, most of the data points are distributed around the 45° line for all other models, which indicates that these multicomponent isotherm models could represent the experimental adsorption data for the binary systems with varying degrees of fit.

The multi-component non-modified Langmuir model shows a poor fit to the experimental data (MPSD = 101.6). All the modified Langmuir coefficients ($\eta_{L,i}$) estimated were much greater than 1.0 indicating that the non-modified multi-component Langmuir model related to the individual

Table 3. Freundlich and Langmuir constants for adsorption of cadmium(II) and zinc(II) on various adsorbents

Adsorbent	K_F (mg/g)/(mg/l)$^{1/n}$	n	q_m (mg/g)	K_L (l/mg)	Reference
Cadmium					
Red mud	–	–	106.45	0.01	(6)
Afsin-Elbistan fly ash	–	–	0.29	179.40	(7)
Seyitomer fly ash	–	–	0.22	11.08	(7)
Akaganeite-type nanocrystals	1.94	0.40	17.10	0.03	(8)
Baker's yeast cells	3.08	1.45	31.75	0.09	(9)
Corncob	3.72	0.08	5.09	1.23	(12)
Corncob (Oxidized 0.6 M CA[a])	26.10	0.19	55.20	0.33	(12)
Corncob (Oxidized 1 M NA[b])	13.50	0.08	19.30	0.57	(12)
Fontinalis antipyretica	–	–	29.00	0.13	(37)
Amberlite IR-120 resin	–	–	101.06	0.01	(38)
Pelvetia caniculata	13.00	0.36	75.00	0.08	(39)
AC[c] from bagasse	5.78	0.28	38.03	13.2	(40)
Bagasse fly ash	0.85	0.47	6.19	0.09	Present work
Zinc					
Kali river bed sediments	0.26	0.31	0.61	0.64	(10)
Dried animal bones	0.34	0.62	12.49	0.28	(11)
Oil shale ash treated with NA[b]	0.002	2.35	–	–	(13)
Oil shale ash treated with NA[b] and NaOH	0.19	2.54	–	–	(13)
Fontinalis antipyretica	–	–	15	0.15	(37)
AC[c] from bagasse	5.62	0.25	31.11	0.01	(40)
AC[c] wood waste (sawdust)	10.05	0.18	18.54	1.41	(41)
F-400 (bituminous carbon)	1.02	0.49	10.62	0.04	(41)
F-300 (bituminous carbon)	1.83	0.29	6.03	0.18	(41)
Centaur HSL (bituminous carbon)	0.81	0.55	10.08	0.04	(41)
Bagasse fly ash	1.43	0.42	7.03	0.18	Present work

[a] CA (Citric acid).
[b] NA (Nitric acid).
[c] AC (Activated Carbon).

isotherm parameters could not be used to predict the binary-system adsorption. However, the use of the interaction term, $\eta_{L,i}$, in the modified Langmuir model (MPSD = 28.3) clearly increased the fit of the non-modified Langmuir model. The use of the multicomponent

Table 4. Comparison of the experimental and calculated q_e values evaluated from the mono-component Langmuir, Freundlich, and Redlich–Peterson models for the individual adsorption of cadmium(II) and zinc(II) to bagasse fly ash

			$q_{e,calc}$ (mg/g)		
C_0 (mg/l)	C_e (mg/l)	$q_{e,\exp}$ (mg/g)	Langmuir	Freundlich	R–P
Cadmium(II)					
10	1.10	0.89	0.56	0.89	0.89
20	3.98	1.60	1.63	1.63	1.65
30	7.46	2.25	2.49	2.19	2.21
50	17.10	3.29	3.75	3.24	3.25
100	48.20	5.18	5.03	5.27	5.23
MPSD			23.89	2.39	2.19
Zinc(II)					
10	0.40	0.96	0.47	0.97	0.96
20	1.80	1.82	1.72	1.82	1.85
30	4.00	2.60	2.94	2.53	2.57
50	11.00	3.90	4.67	3.86	3.87
100	37.30	6.27	6.12	6.40	6.31
MPSD			32.61	2.19	1.18

extended-Langmuir model in the present study shows its inadequacy to represent the experimental data (MPSD values are large). The K_i values, reflecting the affinity between the adsorbent and the metals in the binary systems by using the BFA are 0.04 l/mg for both Cd(II) and Zn(II).

Table 5. Multi-component isotherm parameter values for the simultaneous removal of cadmium(II) and Zinc(II) by bagasse fly ash

	Non-modified Langmuir model		Non-modified R–P model	
MPSD	101.6		52.0	
	Modified Langmuir model	Extended Langmuir model		Modified R–P model
Adsorbate	$\eta_{L,i}$	K_i	$q_{\max}$	$\eta_{R,i}$
Cadmium(II)	1.96	0.04	7.24	0.54
Zinc(II)	1.71	0.04		2.15
MPSD	28.3	28.5		24.1
	SRS Model			
Adsorbate	a_{12}	a_{21}		
Cadmium(II)	1	2.15		
Zinc(II)	2.70	1		
MPSD	15.4			

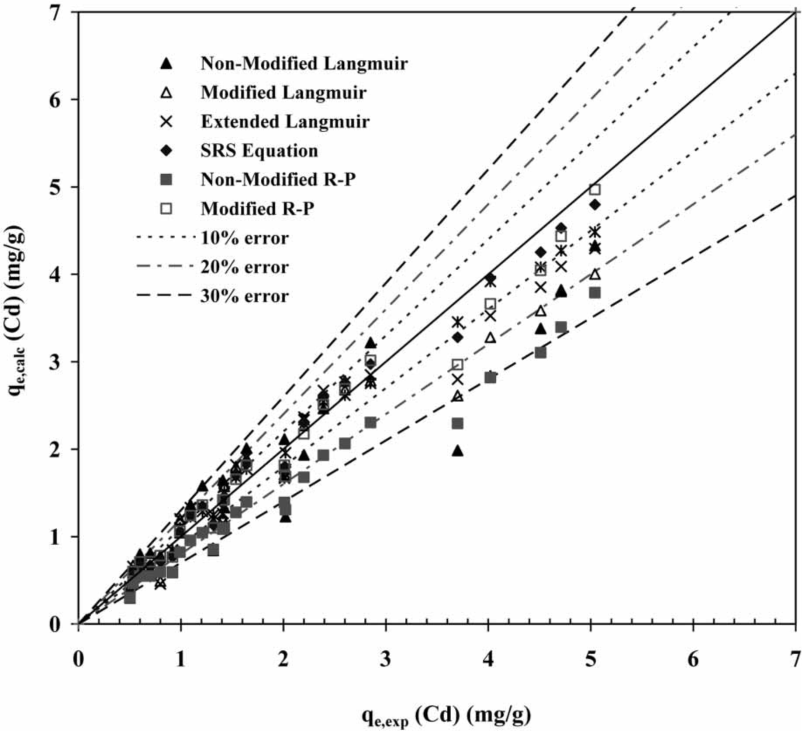

Figure 5. Comparison of the experimental and calculated q_e values of cadmium(II) ions in a binary mixture of cadmium(II) and zinc(II) ions.

The overall total metal ions uptakes ($q_{\max}$) by BFA is 7.24 mg/g. These values are considerably lower than the sum of the maximum total capacities of Cd(II) and Zn(II) ions resulting from the single component adsorption systems. For that reason, the adsorption sites of Cd(II), and Zn(II) in binary systems onto BFA may likely be partially overlapped. It may also imply that there may be a variety of binding sites on the adsorbents showing partially specific to the individual metal ions. The information obtained from the maximum capacities seems to violate the basic assumptions of the Langmuir model, i.e. that the entire adsorbent surface is homogeneous and that there is no lateral interaction between the adsorbate molecules, and thus the affinity of each binding site for the adsorbate molecules should be uniform.

The use of interaction terms, $\eta_{R,i}$, for the modified R–P model (MPSD = 24.1) improved the fit of the non-modified R–P model (MPSD = 52.0), however, the SRS model (MPSD = 15.4) best-fitted to the binary adsorption data of Cd(II) and Zn(II) onto BFA. Thus, the SRS isotherm is the best for representing the binary system adsorption. This is expected as BFA has a heterogeneous surface and the adsorption of the

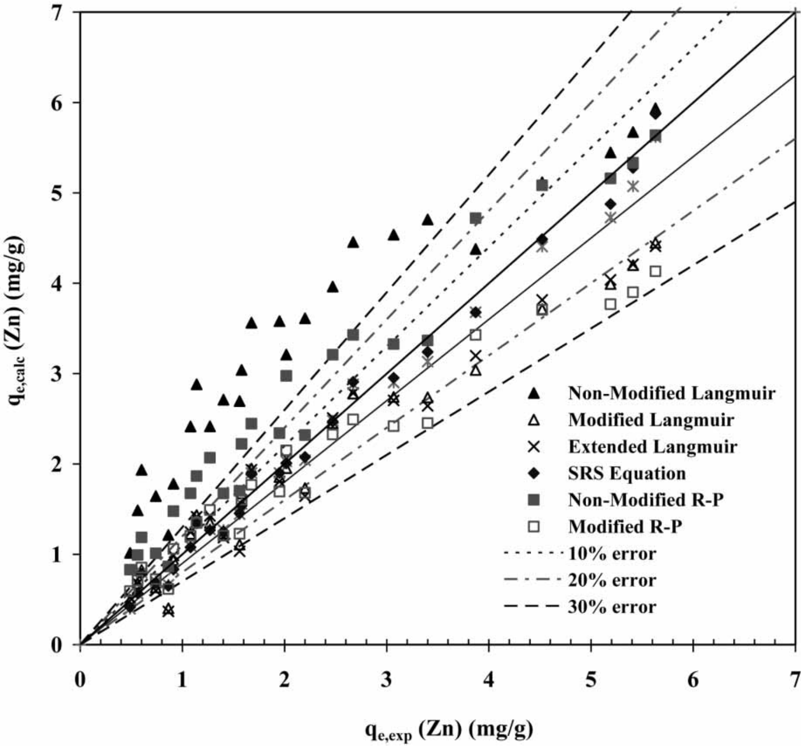

Figure 6. Comparison of the experimental and calculated q_e values of zinc(II) ions in a binary mixture of cadmium(II) and zinc(II) ions.

single metal ions have also been well represented by the Freundlich isotherm equation. It is evident that the modification of the Freundlich equation as given by the SRS model takes into account the interactive effects of individual metal adsorbate ions between and among themselves and the adsorbent reasonably well. Therefore, the binary adsorption of metal ions onto BFA can be represented satisfactorily and adequately by the SRS model.

The multicomponent SRS model applies to those systems where each component individually obeys the single-component Freundlich isotherm. The isotherm coefficients can be determined from the mono-component isotherm except for the adsorption competition coefficients, a_{ij}, which have to be determined experimentally. The competition coefficients, a_{ij}, describe the inhibition to the adsorption of component i by component j. The two components for the present study were found to obey the single-component Freundlich model individually. The competition coefficients a_{ij} and a_{ji} were estimated from the competitive adsorption data of Cd(II), Ni(II), and Zn(II) ions by using MS EXCEL 2002 program. A comparison of the competition coefficients in the adsorption isotherm equation shows that the uptake of the strongly adsorbed Zn(II) was significantly inhibited by the presence of Cd(II) ($a_{21} = 2.70$). Similarly the uptake of Cd(II) by BFA gets suppressed in the presence of Zn(II) ion in the solution ($a_{12} = 2.15$).

Three-dimensional (3-D) adsorption isotherm surfaces are used to evaluate the performance of the binary metal ions adsorption system. The multi-component SRS model can be used to simulate the equilibrium sorption behavior of the ternary metal ions system through 3-D 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 appropriate input equation. The adsorption isotherm surfaces of Cd(II) and Ni(II) for BFA, as shown in Fig. 7, were created by using the multicomponent SRS model and smoothed and fitted to the experimental adsorption data. Depending on the $q_{e,i}$ value calculated and used, there could be two different adsorption-isotherm surface plots:

1. for the uptake of Cd(II), yielding the effect of Zn(II) on Cd(II) (Fig. 7a); and
2. for the uptake of Zn(II), yielding the effect of Cd(II) on Zn(II) (Fig. 7b). When both Zn(II) and Ni(II) ions were present in the solution together, some reduction of the Cd(II) uptake was observed with increasing Zn(II) concentrations (Fig. 7a).

The uptake of Zn(II) ions also decreased with increasing equilibrium Cd(II) concentrations (Fig. 7b). It can be seen in the Fig. 7 that the predictions of SRS model for the simultaneous adsorption of Cd(II) and Zn(II) ions by BFA from aqueous solution are very satisfactory.

CONCLUSION

The present study shows that the bagasse fly ash (BFA) is an effective adsorbent for the removal of Cd(II) and Zn(II) metal ions from the aqueous solution. Maximum sorption for both Cd(II) and Zn(II) metals ions was found to occur at pH_0 6.0. A higher percentage of metal ion removal was possible provided that the initial adsorbate concentration in the solution was low. Freundlich and Redlich–Peterson isotherms show a very good fit with the experimental single component adsorption equilibrium data. The affinity of the BFA for Zn(II) ions was marginally higher than that for Cd(II), from both the single component and the binary solutions under the same experimental conditions. The net interactive effect of Cd(II) and Zn(II) ions on the adsorption of each metal ion by BFA was found to be antagonistic. The simultaneous adsorption phenomena of Cd(II) and Zn(II) ions on the BFA were expressed by various multi-component models. Based on Marquardt's percent standard deviation (MPSD) error function the SRS adsorption isotherm which is based on the Freundlich model showed

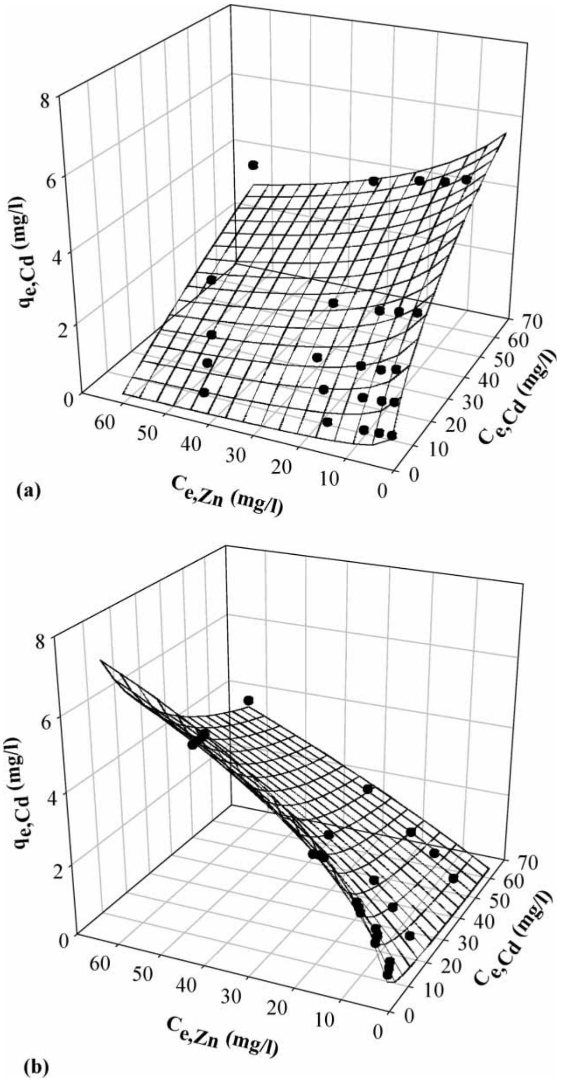

Figure 7. Binary adsorption isotherms cadmium(II)-zinc(II). The surfaces are predicted by the SRS model and the symbols are experimental data. (a) Cadmium(II) uptake and (b) Zinc(II) uptake.

the best fit to the binary adsorption data. The regeneration of the spent BFA is not recommended because of it being a waste material and being available at almost no cost. The desorption experiments with different solvents showed only a partial elution of the metal ions (42). The metal loaded spent BFA can be used for making fire-briquettes and used in the furnaces to recover its energy value. The resultant bottom ash can be blended with cementitious mixture and used as building blocks. Finally, it may be concluded that BFA may be used for the individual and simultaneous removal of Cd(II) and Zn(II) ions from metal-containing effluents.

NOMENCLATURE

a_{ij}	competition coefficients of component i by component j, dimensionless
a_R	constant of Redlich–Peterson isotherm, l/mg
BFA	bagasse fly ash
C_0	initial concentration of adsorbate in solution, mg/l
$C_{0,i}$	initial concentration of each component in solution, mg/l
C_e	unadsorbed concentration of the single-component at equilibrium, mg/l
$C_{e,i}$	unadsorbed concentration of each component in the binary mixture at equilibrium, mg/l
k_S	rate constant of pseudo-second-order adsorption model, g/mg min
K_i	individual extended Langmuir isotherm constant of each component, l/mg
K_F	mono-component (non-competitive) constant of Freundlich isotherm of the single component, $(\mathrm{mg/g})/(\mathrm{l/mg})^{1/\mathrm{n}}$
$K_{F,i}$	individual Freundlich isotherm constant of each component, $(\mathrm{mg/g})/(\mathrm{l/mg})^{1/\mathrm{n}}$
K_L	constant of Langmuir isotherm, l/mg
$K_{L,i}$	individual Langmuir isotherm constant of each component, l/mg
K_R	constant of Redlich–Peterson isotherm, l/g
m	mass of adsorbent per liter of solution, g/l
n_m	number of measurements
n_p	number of parameters
n	mono-component (non-competitive) Freundlich heterogeneity factor of the single component, dimensionless
n_i	individual Freundlich heterogeneity factor of each component, dimensionless
N	number of data points
$N_i(Q)$	Number of sites having energy Q, dimensionless
pH_0	initial pH of the solution
MPSD	Marquardt's percent standard deviation
q_e	equilibrium single-component solid phase concentration, mg/g
$q_{e,i}$	equilibrium solid phase concentration of each component in binary mixture, mg/g
$q_{e,cal}$	calculated value of solid phase concentration of adsorbate at equilibrium, mg/g
$q_{e,\mathrm{exp}}$	experimental value of solid phase concentration of adsorbate at equilibrium, mg/g

q_m	maximum adsorption capacity of adsorbent, mg/g
$q_{\max}$	constant in extended Langmuir isotherm, mg/g
Q	adsorption energy, J
R	universal gas constant, 8.314 J/K mol
t	time, min
T	absolute temperature, K
X_{Ae}	fraction of the adsorbate adsorbed on the adsorbent under equilibrium

Greek Symbols

α_i	constant in SRS model for each component, dimensionless
β	constant of Redlich–Peterson isotherm ($0 < \beta < 1$)
β	constant in SRS model for each component, dimensionless
$\eta_{L,i}$	multi-component (competitive) Langmuir adsorption constant of each component, dimensionless
$\eta_{R,i}$	multi-component (competitive) R–P adsorption constant of each component, dimensionless
$\theta_i(Q)$	coverage of each component at energy level Q, dimensionless

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