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Equilibrium modelling of single and binary adsorption of cadmium and nickel onto bagasse fly ash

Vimal Chandra Srivastava, Indra Deo Mall *, Indra Mani Mishra

Department of Chemical Engineering, Indian Institute of Technology, Roorkee, Roorkee 247667, India

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Abstract

The present study deals with the competitive adsorption of cadmium (Cd(II)) and nickel (Ni(II)) ions onto bagasse fly ash (BFA) from single component and binary systems. BFA is a waste material obtained from the flue gas of the bagasse-fired boilers of sugar mills. Equilibrium adsorption is affected by the initial pH (pH_0) of the solution. The $pH_0 \approx 6.0$ is found to be the optimum for the individual removal of Cd(II) and Ni(II) ions by BFA. The pH of the system, however, increases during the initial sorption process for about 20 min and, thereafter, it remains constant. The equilibrium adsorption data were obtained at different initial concentrations (C_0 = 10–100 mg/l), 5 h contact time, 30 °C temperature, BFA dosage of 10 mg/l at pH_0 6. The single ion equilibrium adsorption data were fitted to the non-competitive Langmuir, Freundlich and Redlich–Peterson (R–P) isotherm models. The R–P and the Freundlich models represent the equilibrium data better than the Langmuir model in the studied initial metal concentration range (10–100 mg/l). The adsorption capacity of Ni(II) is higher than that for Cd(II) for the binary metal solutions 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 Ni(II) ions on BFA is generally found to be antagonistic. Equilibrium isotherms for the binary adsorption of Cd(II) and Ni(II) ions onto BFA have been analyzed by using non-modified Langmuir, modified Langmuir, extended Langmuir, extended Freundlich and Sheindorf–Rebuhn–Sheintuch (SRS) models. The competitive extended Freundlich model fits the binary adsorption equilibrium data satisfactorily and adequately. Desorption with various solvents showed that the hydrochloric acid is the best solvent; the maximum elution being about 65% for Cd(II) and about 42% for Ni(II). Since BFA is a waste material obtained at almost no cost, the spent BFA can be combusted to recover its energy value and the bottom ash can be blended with cementitious mixture for making building blocks.

Keywords: Binary adsorption; Bagasse fly ash (BFA); Simultaneous metal removal; Multi-component isotherms; Cadmium(II); Nickel(II)

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1. Introduction

Heavy metals are widely distributed in the environment and are biologically significant due to their toxicity. They are non-biodegradable and their concentration gets accentuated through bioaccumulation via food chain in living tissues, causing various diseases and disorders. Cadmium occurs in nature in the form of cadmium sulfide (CdS), usually as a minor component in zinc, lead and copper ores. During metal extraction and refining in zinc, lead and copper smelters, cadmium gets reduced in the environment in the form of metal slag and dissolved form in wastewaters. Several noxious effects have been attributed to cadmium in living systems, e.g. isomorphic substitution of zinc(II) (in enzymes, with their consequent damage) and of cadmium (in bone tissues, which are fragilized) [1]. Cadmium is known to get accumulated in the kidneys causing 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]. Nickel is also a common environmental pollutant which is considered as toxic (e.g. in concentrations of 15 mg/l), especially to activated sludge bacteria, and its presence is detrimental to the operation of anaerobic digesters used in wastewater treatment plants [4]. Cadmium (Cd(II)) and nickel (Ni(II)) ions are frequently encountered together in industrial wastewaters (e.g. from mine drainage, plating plants, paint and ink formulation units, and porcelain enamelling). Nickel concentration in wastewaters varies from a low value of 0.5 mg/l to a high value of 1000 mg/l. However, the average concentration in the effluent from the plating plants ranges between 10 and 80 mg/l. Average cadmium ion concentration from plating plants is generally

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* Corresponding author. Tel.: +91 1332 285319 (O), +91 1332 285106 (R); fax: +91 1332 276535/273560.

E-mail address: id_mall2000@yahoo.co.in (I.D. Mall).

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Nomenclature

a_{ij}	competition coefficients of component i by component j
a_R	constant of Redlich–Peterson isotherm (l/mg)
BFA	bagasse fly ash
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)
C_0	initial concentration of adsorbate in solution (mg/l)
$C_{0,i}$	initial concentration of each component in solution (mg/l)
K_F	mono-component (non-competitive) constant of Freundlich isotherm of the single component ((mg/g)/(l/mg)$^{1/n}$)
$K_{F,i}$	individual Freundlich isotherm constant of each component ((mg/g)/(l/mg)$^{1/n}$)
K_i	individual extended Langmuir isotherm constant of each component (l/mg)
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)
MPSD	Marquardt's percent standard deviation
n	mono-component (non-competitive) Freundlich heterogeneity factor of the single component
n_i	individual Freundlich heterogeneity factor of each component
n_m	number of measurements
n_p	number of parameters
N	number of data points
$N_i(Q)$	number of sites having energy Q
pH_0	initial pH of the solution
q_e	equilibrium single-component solid phase concentration (mg/g)
$q_{e,cal}$	calculated value of solid phase concentration of adsorbate at equilibrium (mg/g)
$q_{e,exp}$	experimental value of solid phase concentration of adsorbate at equilibrium (mg/g)
$q_{e,i}$	equilibrium solid phase concentration of each component in binary mixture (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_i, y_i, z_i	multi-component (competitive) Freundlich adsorption constants of each component
X_{Ae}	fraction of the adsorbate adsorbed on the adsorbent under equilibrium

Greek letters

α_i	constant in SRS model for each component
β	constant of Redlich–Peterson isotherm ($0 < \beta < 1$)
β_i	constant in SRS model for each component
η_i	multi-component (competitive) Langmuir adsorption constant of each component
$\theta_i(Q)$	coverage of each component at energy level Q

around 15–20 mg/l. In lead mine acid drainage, the concentration can be as high as 1000 mg/l. 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 2.0 mg/l, respectively, for Cd(II) and Ni(II) for safe discharge of the effluents containing these metal ions into surface waters [5].

The methods used for the removal of metals from wastewaters include chemical precipitation, membrane filtration, ion exchange and adsorption. Precipitation methods are particularly reliable but require large settling tanks for the precipitation of voluminous alkaline sludge and a subsequent treatment is also needed [6]. Ion exchange has the advantage of allowing the recovery of metallic ions, but it is expensive and sophisticated. Adsorption as a wastewater treatment process has aroused considerable interest during recent years. Commercially activated carbon is regarded as the most effective adsorbent for controlling the organic and inorganic load. However, due to its high cost and about 10–15% loss during regeneration, unconventional adsorbents like bagasse fly ash (BFA), peat, lignite, bagasse pith, wood, saw dust, etc. have attracted the attention of several investigators. Utilization of various low-cost adsorbents for the removal of heavy metals and other pollutants has been recently presented by Mall et al. [7] and Bailey et al. [8].

The sugar industry is one of the most important agri-based industries in India, South America and Caribbean countries. BFA is a waste collected from the particulate collection equipment attached upstream to the stacks of bagasse-fired boilers. 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 colour from sugar mill [9] and paper mill effluents [10]. Various researchers have utilized it for the adsorptive removal of phenolic compounds [11,12] and dyes [13–15]. BFA is available in plenty and has no cost. Most of the sugar mills spend money on its collection, transportation and disposal as a land-fill material. Therefore, its use in adsorption will not entail any expenditure, excepting that on its transportation, sieving and final disposal. Thus, the adsorption with BFA may prove to be much cheaper than that with activated carbon.

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 is very important. The equilibrium adsorption isotherm equations proposed for single-component adsorption have been extended and modified to represent the binary and multi-component adsorption equilibria. However, no information is available in literature for the simultaneous removal of Cd(II) and Ni(II) ions by BFA.

The aim of the present paper is to (i) study the feasibility of using BFA as an adsorbent for the individual and simultaneous removal of Cd(II) and Ni(II) metal ions from aqueous solutions, (ii) study the effect of initial pH (pH_0) on the adsorption process and the pH change during the process, (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 Ni(II) ions and (v) to examine the applicability of the multi-component adsorption isotherm equations to the competitive adsorption equilibria of the metals in a binary system.

2. Theory

2.1. Mono-component 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 [16] is derived by assuming a heterogeneous surface with a non-uniform distribution of heat of adsorption over the surface. Whereas in the Langmuir theory [17], the basic assumption is that the sorption takes place at specific homogeneous sites within the adsorbent. The R–P isotherm [18] can be described as follows:

$$q_\mathrm{e} = \frac{K_\mathrm{R} C_\mathrm{e}}{1 + a_\mathrm{R} C_\mathrm{e}^{\beta}} \tag{1}$$

where K_R is the R–P isotherm constant (l/g), a_R is also a constant having unit of $(\mathrm{l/mg})^{\beta}$ and β is an exponent having a value between 0 and 1. C_e is the equilibrium liquid-phase concentration of the adsorbate (mg/l) and q_e is the equilibrium adsorbate loading onto the adsorbent (mg/g).

At high liquid-phase concentrations of the adsorbate, Eq. (1) reduces to the Freundlich equation, i.e.

$$q_\mathrm{e} = K_\mathrm{F} C_\mathrm{e}^{1/n} \quad \text{or} \quad \ln q_\mathrm{e} = \ln K_\mathrm{F} + n \ln C_\mathrm{e} \tag{2}$$

where $K_\mathrm{F} = K_\mathrm{R}/a_\mathrm{R}$, if $\beta = 1$, is the Freundlich constant $\lfloor(\mathrm{l/mg}^{n-1})^{1/n}/\mathrm{g}\rfloor$ and $(1/n) = (1 - \beta)$ is the heterogeneity factor.

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

$$q_\mathrm{e} = \frac{q_\mathrm{m} K_\mathrm{L} C_\mathrm{e}}{1 + K_\mathrm{L} C_\mathrm{e}} \quad \text{or} \quad \frac{C_\mathrm{e}}{q_\mathrm{e}} = \frac{C_\mathrm{e}}{q_\mathrm{m}} + \frac{1}{K_\mathrm{L} q_\mathrm{m}} \tag{3}$$

where K_L ($=a_\mathrm{R}$) is the Langmuir adsorption constant (l/mg) related to the energy of adsorption and q_m ($=K_\mathrm{R}/a_\mathrm{R}$) signifies the adsorption capacity of the adsorbent (mg/g).

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

$$q_\mathrm{e} = \frac{K_\mathrm{R} C_\mathrm{e}}{1 + a_\mathrm{R}} = K_\mathrm{H} C_\mathrm{e} \tag{4}$$

where K_H is the Henry's constant (l/g).

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

$$\ln\left(K_\mathrm{R}\frac{C_\mathrm{e}}{q_\mathrm{e}} - 1\right) = \ln a_\mathrm{R} + \beta \ln C_\mathrm{e} \tag{5}$$

A minimization procedure can be 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.

2.2. Multi-component isotherm equations

2.2.1. Non-modified competitive Langmuir model

Writing the basic Langmuir model for component i in a N-component system wherein competitive adsorption takes place, one gets:

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

where $q_{\mathrm{m},i}$ and $K_{\mathrm{L},i}$ can be estimated from the fitting of the experimental data by the corresponding individual Langmuir isotherm equations.

2.2.2. Modified competitive Langmuir isotherm [19]

Individual adsorption constants may not describe the interactions between individual metal ions as also between an individual metal ion and the mixture. The interactive effect can be incorporated in the individual isotherm equations by correcting the individual adsorbate concentration by an interaction term, η_i, as given in Eq. (7). η_i is a characteristic of each species and depends on the concentrations of the other components in the solution. η_i can be estimated from the competitive adsorption data. The modified competitive Langmuir isotherm equation is given as

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

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

2.2.3. *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, Yang [20] extended the Langmuir equation for multi-component systems as

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

Here, the values of $q_{\max}$ and K_i can be obtained from the optimized fitting of Eq. (8) with the experimental data for the equilibrium adsorption of components in the multi-component system.

2.2.4. *Extended Freundlich isotherm*

The equilibrium adsorption from binary mixtures can also be represented by the extended Freundlich equation as given below [21]:

$$q_{e,1} = \frac{K_{F,1} C_{e,1}^{n_1+x_1}}{C_{e,1}^{x_1} + y_1 C_{e,2}^{z_1}} \tag{9}$$

$$q_{e,2} = \frac{K_{F,2} C_{e,2}^{n_2+x_2}}{C_{e,2}^{x_2} + y_2 C_{e,1}^{z_2}} \tag{10}$$

where $K_{F,1}$, $K_{F,2}$, n_1 and n_2 can be estimated from the corresponding individual Freundlich isotherm equations and the other six parameters (x_1; y_1; z_1 and x_2; y_2; z_2) are the multi-component Freundlich adsorption constants of the first and the second components [22].

2.2.5. *Sheindorf–Rebuhn–Sheintuch (SRS) equation*

Sheindorf et al. [23] derived a Freundlich-type multi-component adsorption isotherm equation known as the Sheindorf–Rebuhn–Sheintuch equation, to represent the experimental data. The general SRS equation for a component *i* in an *N*-component system is given as:

$$q_{e,i} = K_{F,i} C_{e,i} \left(\sum_{j=1}^{N} a_{ij} C_{e,j} \right)^{n_i - 1} \tag{11}$$

The constant $K_{F,i}$ and the exponent n_i are determined from the single-component equilibrium adsorption data. The competition coefficients a_{ij} account for the inhibition to the adsorption of the component *i* by the component *j*, and can be determined from the thermodynamic data, or more likely, from the experimental adsorption data of the multi-component system. The SRS equation assumes that in a multi-component adsorption system, (i) each component individually obeys the Freundlich isotherm; (ii) for each component, there exists an exponential distribution of site adsorption energies, i.e.

$$N_1(Q) = \alpha_i \exp\left(-\frac{\beta_i Q}{RT} \right) \tag{12}$$

where α_i and β_i are constants; (iii) the surface coverage θ_i by each adsorbate molecule (or ion) at each energy level Q is given by the multi-component Langmuir isotherm equation, i.e.

$$\theta_i(Q) = \frac{K_i C_{e,i}}{1 + \sum_{j=1}^{N} K_j C_{e,j}} \tag{13}$$

where

$$K_j = K_{0j} \exp\left(\frac{Q}{RT} \right) \tag{14}$$

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 multi-component equilibrium adsorption of different types of contaminants [23–26].

The $q_{e,i}$, individual adsorption yield ($\text{Ad}_i\%$) and the total adsorption yield ($\text{Ad}_{\text{Tot}}\%$) can be calculated by using the following expressions:

$$q_{e,i} = \frac{(C_{0,i} - C_{e,i})V}{w} \quad \text{(mg of adsorbate/g of adsorbent)} \tag{15}$$

$$\text{Ad}_i\% = \frac{100(C_{0,i} - C_{e,i})}{C_{0,i}} \tag{16}$$

$$\text{Ad}_{\text{Tot}}\% = \frac{100 \sum (C_{0,i} - C_{e,i})}{\sum C_{0,i}} \tag{17}$$

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

2.3. *Determination of isotherm parameters*

The isotherm parameters of all the multi-component models can be found by using the MS Excel 2002 for Windows by minimizing Marquardt's percent standard deviation (MPSD) [27]. MPSD has been used to test the adequacy and accuracy of the fit of various isotherm models with the experimental data [13,14]. It is similar to the geometric mean error distribution, but modified by incorporating the number of degrees of freedom. MPSD is given as

$$\text{MPSD} = 100 \sqrt{\frac{1}{n_m - n_p} \sum_{i=1}^{n} \left(\frac{q_{e,i,\exp} - q_{e,i,\text{cal}}}{q_{e,i,\exp}} \right)^2} \tag{18}$$

where n_m is the number of experimental data points and n_p is the number of parameters in the isotherm equation.

3. Experimental

3.1. *BFA*

BFA was obtained from a nearby sugar mill (Deoband Sugar Mill, U.P., India) and used as an adsorbent without any pretreatment. Detailed physico-chemical characteristics of the BFA have already been presented elsewhere [10,14]. Proximate analysis was carried out by using the procedure as detailed in IS:1350 (Part I) [28]. Bulk density was determined by using MAC bulk density meter whereas particle size analysis was carried out using standard sieves. Moisture content, volatile matter, ash, fixed carbon and bulk density of BFA were 7.64%, 17.37%, 26.43%, 48.56% and 133.3 kg/m^3, respectively. The particle sizes of BFA were <180 (31.71%), 180–212 (39.92%), 212–850 (21.95%), 850–1000 (1.97%), 1000–1180 (2.09%), 1180–1400 (1.40%) and >1400 (0.96%) μm. X-ray diffraction analysis of BFA was carried out using Phillips (Holland) diffraction unit (Model PW 1140/90), using copper target with nickel as filter media, and K radiation maintained at 1.542 Å. Goniometer speed was maintained at 1°/min. X-ray spectrum of BFA reflects the presence of alumina (Al_2O_3), silica (SiO_2), CaO, $CaSiO_3$ and $Ca_8Si_5O_{18}$. Diffraction peaks corresponding to crystalline carbon were not observed in BFA.

The specific surface area was measured by N_2 adsorption isotherm using an ASAP 2010 Micromeritics instrument and by Brunauer–Emmett–Teller (BET) method, using the software of Micromeritics. Nitrogen was used as cold bath (77.15 K). The Barrett–Joyner–Halenda (BJH) method [29] was used to calculate the mesopore distribution for the BFA. The BET surface area is 168.8 m^2 g^{-1} whereas BJH adsorption/desorption surface area of pores is 54.2/49.9 m^2 g^{-1}. The single point total pore volume of pores (d < 1042.3 Å) is 0.101 cm^3 g^{-1}, whereas cumulative pore volume of pores (17 Å < d < 3000 Å) is 0.053 cm^3 g^{-1}. The analysis of the BJH adsorption pore distribution shows that the mesopores (20 Å < d < 500 Å) have a total pore area of about 99% and that the macropores about 1%. The average pore diameter by BET method is found to be 23.97 Å, whereas the BJH adsorption/desorption average pore diameter is 39.36 Å/33.90 Å. The BFA, thus, is found to consist of mesopores predominantly. This is what is desirable for the liquid-phase adsorptive removal of metal ions.

FTIR spectrometer (Thermo Nicolet, Model Magna 760) was employed to determine the presence of functional groups in BFA at room temperature. Pellet (pressed-disk) technique was used for this purpose. The pellets were prepared by using the same ratio of each adsorbent in KBr. The spectral range was from 4000 to 400 cm^{-1}. According to FTIR spectra, a broad band between 3100 and 3700 cm^{-1} in BFA indicated the presence of both free and hydrogen bonded OH groups on the adsorbent surface [30]. This stretching is due to both the silanol groups (Si–OH) and adsorbed water (peak at 3400 cm^{-1}) on the surface [31]. The stretching of the OH groups bound to methyl radicals presented a very light signal ~2920 cm^{-1} for BFA. The spectra indicated weak and broad peaks in the region of 1600–1800 cm^{-1} corresponding to CO group stretching from aldehydes and ketones. The FTIR spectra of BFA showed transmittance in the 1050–1290 cm^{-1} region due to the vibration of the CO group in lactones [32]. The 1360–1380 cm^{-1} band may be attributed to the aromatic CH and carboxyl–carbonate structures [33]. The peak at 1100 cm^{-1} is due to –C–O–H stretching and –OH deformation values, while the peak at 1620 cm^{-1} may be due to NH deformation. Although some inference can be drawn about the surface functional groups from IR spectra, the weak and broad bands do not provide any authentic information about the nature of the surface oxides. The presence of polar groups on the surface [34] is likely to give considerable cation exchange capacity to the adsorbents.

3.2. Chemicals

All the chemicals used in the study were of analytical reagent (AR) grade. Nickel chloride hexahydrate ($NiCl_2 \cdot 6H_2O$) was procured from M/S Qualigens Fine Chemicals, Mumbai. Cadmium sulphate octahydrate ($CdSO_4 \cdot 8H_2O$), NaOH and HCl were obtained from s.d. Fine Chemicals, Mumbai. Stock solutions of Cd(II) and Ni(II) were made by dissolving exact amount of $CdSO_4 \cdot 8H_2O$ and $NiCl_2 \cdot 6H_2O$ in distilled water, respectively. The range of concentration of both components prepared from stock solution varied between 10 and 100 mg/l. These test solutions were prepared by diluting 1 g/l of stock solution of Cd(II) and Ni(II) with double-distilled water. The acids used in the desorption studies were obtained from s.d. Fine Chemicals.

3.3. Batch adsorption and desorption studies

For each experimental run, 100 ml aqueous solution of the known concentration of Cd(II), Ni(II) or a 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 of the adsorbate solution is affected by the addition of the BFA. The sorption process is affected by the initial pH (pH_0) of the adsorbate solution–adsorbent mixture. During the process of sorption, pH changes continuously. Therefore, the effect of pH_0 on the sorption was studied by adjusting the pH_0 in the range of 2–10 using 1N (36.5 g/l) HCl or 1N (40 g/l) NaOH aqueous solution. In these experiments, the BFA loading was kept at 10 g/l of the adsorbate solution containing 30 mg/l each of Cd(II) and Ni(II) at 30 °C. Since it was found that the equilibrium between the adsorbate concentration in the adsorbent and in the solution was attained in 5 h, the effect of pH_0 on the extent of adsorption was estimated after 5 h of the mixing of the adsorbate solution and BFA.

Cd(II) and Ni(II) in the sample was determined by flame atomic absorption spectrophotometer (GBC Avanta, Australia) with the detection limit of 0.009 for Cd(II) and 0.040 mg/l for Ni(II) at the wavelength of 228.8 and 232 nm, for Cd(II) and Ni(II), respectively, by using air-acetylene flame. Before the analysis, the sample was diluted to the concentration in the range of 0.2–1.8 and 1.8–8 mg/l for Cd(II) and Ni(II), respectively, with double-distilled water. Metal ion concentrations were determined with reference to appropriate standard metal ion solutions.

3.4. Adsorption isotherm experiments

For single metal–BFA systems, initial metal ion concentration was varied from 10 to 100 mg/l. In binary metal ion mixture–BFA systems, for each initial concentration of Cd(II) solution, viz., 10, 20, 30, 50 and 100 mg/l, the nickel 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 carried out to determine the effect of pH_0 on adsorption capacity of BFA for metal ions. For batch desorption experiments, a series of 250 ml Erlenmeyer flasks containing 50 ml of aqueous solution of HCl, H_2SO_4, HNO_3 and CH_3COOH of known concentration or water was contacted with metal loaded adorbent (0.5 g) at $30 \pm 1\,^{\circ}C$. The mixtures were agitated at 150 rpm for 5 h in the orbital shaker. Thereafter, the supernatant was analyzed for metal ions released into the solvent.

4. Results and discussion

4.1. Effect of initial pH (pH_0)

The pH of the adsorbate solution has significant effect on the sorption of adsorbates on different adsorbents. This is partly due to the fact that the hydrogen ion itself is a strong competing adsorbate, and partly due to the chemical speciation of metal ions under the influence of the solution pH. It is known that cadmium species are present in deionized water in the forms of Cd^{2+}, $Cd(OH)^+$, $Cd(OH)_2{}^0$, $Cd(OH)_{2(S)}$, etc. [35]. The concentration of the hydrolyzed cadmium species depends on the cadmium concentration, and the solution pH. The distribution of various hydrolyzed Cd^{2+} species as a function of pH is presented in Fig. 1. The percentage of Cd^{2+} hydrolytic products was calculated from the following stability constants [36]:

$$Cd^{2+} + H_2O \rightleftharpoons Cd(OH)^+ + H^+, \quad pK_1 = 7.9$$

$$Cd(OH)^+ + H_2O \rightleftharpoons Cd(OH)_2 + H^+, \quad pK_2 = 10.6$$

$$Cd(OH)_2 + H_2O \rightleftharpoons Cd(OH)_3{}^- + H^+, \quad pK_3 = 14.3$$

It is evident that the Cd^{2+} ions are the only ionic species present in the solution for $pH < 6$. It is obvious that in the alkaline range precipitation plays main role in removing the Cd(II) ions attributed to the formation of precipitate of $Cd(OH)_{2(S)}$. Similarly, species diagram constructed by Mavros et al. [37] showed that Ni(II) are the only ions present in the nickel solution at $pH < 6$. The precipitation of Ni(II) as $Ni(OH)_2$ precipitate takes place at $pH > 7.7$. This is also confirmed in the present study and those of other investigators [38,39].

During the adsorption run, the pH changes quickly and then remains constant. For a typical experimental run, the time course of pH is shown in Fig. 2. It can be seen from Fig. 2 that the pH of the adsorbate solution increases from pH_0 6 to a final of 8.40 for Cd(II) and 8.31 for Ni within a very short time of about 20 min. This increase in pH during the sorption process because of the simultaneous and, perhaps, competitive adsorption of the metal cations and H^+ ions onto BFA. Between pH 6 and 8.5, the majority of Cd is present as $Cd(OH)^+$. The pH seems to remain constant after 3 h of contact between the adsorbate solution and the adsorbent.

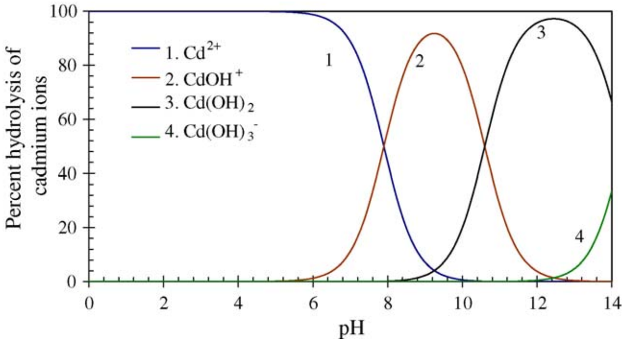

Fig. 1. Distribution of various Cd^{2+} species as a function of pH.

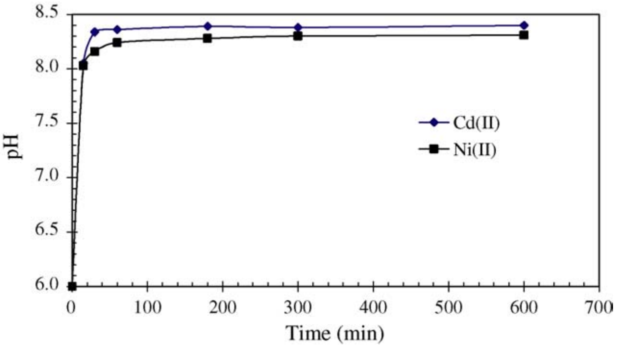

Fig. 2. Variation of pH with time for the removal of Cd(II) and Ni(II) by BFA. pH_0 6.0, $T = 30\,^{\circ}C$, $C_0 = 30$ mg/l, BFA dosage = 10 g/l.

The effect of pH_0 on the removal of individual Cd(II) and Ni(II) ions by BFA is shown in Fig. 3. The removal of metal ions is found to increase with an increase in the pH_0 from 3 to 6. The maximum uptake of metal ions was obtained at about pH_0 6 and the metal ions removal was nearly constant for $pH_0 > 6$.

The oxides of alumina, calcium and silica present in the BFA develop charges in contact with water. Except silica, all other oxides possess positive charge for the pH range of interest because the 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 the aqua complex formation of the oxides present as follows:

$$-\text{MO} + \text{H–OH} \xrightarrow{H^+} \text{M–OH}^{2+} + \text{OH}^- \qquad (19)$$

Cd(II) and Ni(II) ion adsorption at low pH_0 ($pH_0 \leq 6$) is lesser than that at higher pH_0 (≥ 6). 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 $pH_0 < 6$, a significant electrostatic repulsion exists between the positively charged surface

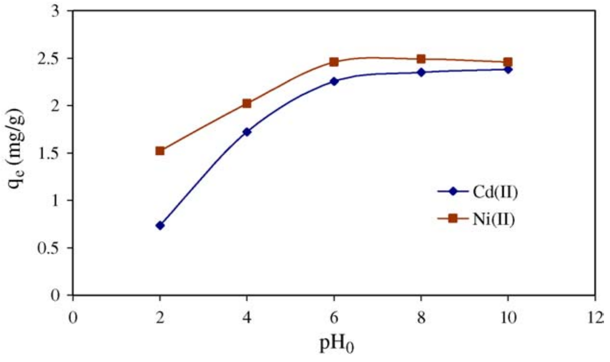

Fig. 3. Effect of pH_0 on the removal of cadmium(II) and nickel(II) ions for single adsorbate aqueous solution by BFA. pH_0 6.0, $T = 30\,^{\circ}C$, $t = 5$ h, $C_0 = 30$ mg/l, BFA dosage = 10 g/l.

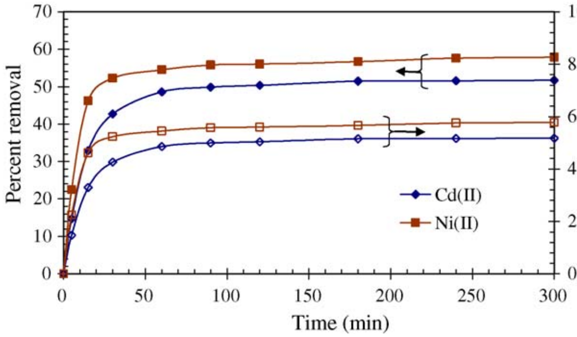

Fig. 4. Effect of contact time on the removal of Cd(II) and Ni(II) by BFA. pH_0 6.0, $T = 30\,^{\circ}C$, $t = 5$ h, $C_0 = 100$ mg/l, BFA dosage = 10 g/l.

of the BFA and the cationic metal ions. Besides, a higher concentration of H^+ in the solution competes with Cd(II) and Ni(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:

$$-\mathrm{MOH} + \mathrm{OH}^- \rightarrow -\mathrm{MO}^- + \mathrm{H_2O} \quad (20)$$

$$-\mathrm{MO}^- + \mathrm{Cd} \rightarrow -\mathrm{M{-}O{-}Cd} \quad (21)$$

A negatively charged surface site on the BFA favours the adsorption of cationic metal ions due to electrostatic attraction. Similar theories have been proposed by Viraraghavan and Rao [40] and Mathialagan and Viraraghavan [41] for metal adsorption on coal fly ash.

4.2. Effect of contact time

Aqueous metal ion solutions with $C_0 = 100$ mg/l were kept in contact with the BFA for 24 h. The residual concentrations at 5 h contact time were found to be higher by a maximum of ∼1% than those obtained after 24 h contact time. Therefore, after 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 under vigorous shaking conditions. Fig. 4 presents the time-course of adsorptive removal of Cd(II) and Ni(II) and their uptake by BFA. The rate of cation removal is found to be very rapid during the initial 20 min, and thereafter, the rate of metal ions removal decreases considerably. No significant change in metal ion removal is observed after about 120 min. It is also found that the adsorptive removal of the metal ions ceases after 300 min of contacting with the BFA. During the initial stage of sorption, a large number of vacant surface sites are available for adsorption. After a lapse of some time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the adsorbate molecules on the solid surface and in the bulk phase. Besides, the metal ions are adsorbed into the mesopores that get almost saturated with metal ions during the initial stage of adsorption. Thus, the driving force for mass transfer between the bulk liquid phase and the solid phase decreases with the passage of time. Further, the metal ions have to traverse farther and deeper into the pores encountering much larger resistance. This results in the slowing down of the adsorption during the later phase of adsorption.

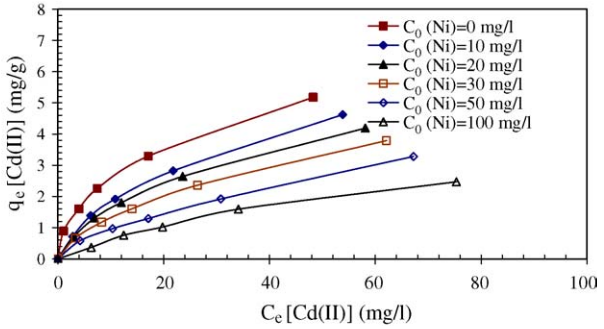

Fig. 5. Comparison of non-linearized adsorption isotherms of cadmium(II) ion in the presence of increasing concentration of nickel(II) ion. pH_0 6.0, $T = 30\,^{\circ}C$, $t = 5$ h, C_0 [Cd(II)] = 10–100 mg/l, BFA dosage = 10 g/l.

4.3. Single and binary adsorption of cadmium(II) and nickel(II) ions

The equilibrium uptakes and the adsorption yields obtained for single-component (Cd(II) and Ni(II)) solutions at pH_0 6.0 are shown in Figs. 5 and 6 and in Table 1. As seen from the figures and the table, the adsorption capacity of BFA for Ni(II) is generally greater than that for cadmium. An increase in the initial metal concentration up to 100 mg/l results in an increase in the equilibrium uptake and a decrease in the adsorption yield of both the components. When the initial ion concentration increases from 10 to 100 mg/l, the loading capacity of BFA increases from 0.89 to 5.18 mg/g for Cd(II) and from 0.95 to 5.78 mg/g for Ni(II). The initial concentration provides the necessary driving force to overcome the resistances to the mass transfer of Cd(II) and Ni(II) ions between the aqueous phases and the solid phase. The increase in the initial concentration also enhances the interaction between the metal ions in the aqueous phase and the BFA. Therefore, an increase in the initial concentration of metal ions enhances the adsorption uptake of Cd(II) and Ni(II) ions. The simultaneous adsorption of Cd(II) and Ni(II) ions from binary mixtures was also investigated at pH_0 6.0. In the first stage of adsorption studies, the initial Cd(II)

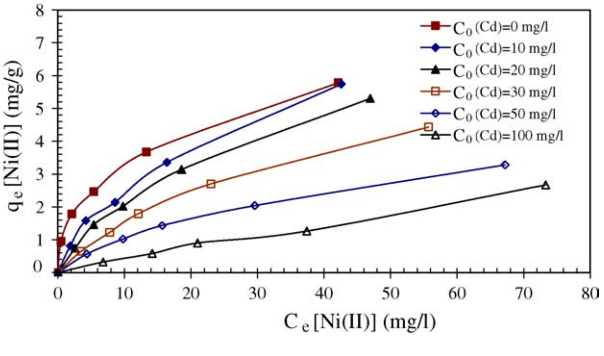

Fig. 6. Comparison of non-linearized adsorption isotherms of nickel(II) ion in the presence of increasing concentration of cadmium(II) ion. pH_0 6.0, $T = 30\,^{\circ}C$, $t = 5$ h, C_0 [Ni(II)] = 10–100 mg/l, BFA dosage = 10 g/l.

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 nickel(II) ions onto bagasse fly ash

$C_{0,\mathrm{Cd}}$	$C_{0,\mathrm{Ni}}$	$C_{e,\mathrm{Cd}}$	$C_{e,\mathrm{Ni}}$	$q_{e,\mathrm{Cd}}$	$q_{e,\mathrm{Ni}}$	$\mathrm{Ad}_{\mathrm{Cd}}$%	$\mathrm{Ad}_{\mathrm{Ni}}$%	$\mathrm{Ad}_{\mathrm{Tot}}$%
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	0.48	0	0.95	0	95.20	95.20
10	10	2.82	1.87	0.72	0.81	71.80	81.30	76.55
20	10	6.20	2.60	1.38	0.74	69.00	74.00	70.67
30	10	10.82	3.52	1.92	0.65	63.93	64.80	64.15
50	10	21.80	4.36	2.82	0.56	56.40	56.40	56.40
100	10	53.80	6.80	4.62	0.32	46.20	32.00	44.91
0	20	0	2.12	0	1.79	0	89.39	89.39
10	20	2.99	4.20	0.70	1.58	70.10	79.00	76.03
20	20	6.95	5.40	1.31	1.46	65.25	73.00	69.13
30	20	12.00	7.80	1.80	1.22	60.00	61.00	60.40
50	20	23.60	9.80	2.64	1.02	52.80	51.00	52.29
100	20	58.10	14.20	4.19	0.58	41.90	29.00	39.75
0	30	0	5.41	0	2.46	0	81.98	81.98
10	30	3.33	8.60	0.67	2.14	66.70	71.33	70.18
20	30	8.28	9.80	1.17	2.02	58.60	67.33	63.84
30	30	14.00	12.10	1.60	1.79	53.33	59.67	56.50
50	30	26.40	15.70	2.36	1.43	47.20	47.67	47.38
100	30	62.10	21.00	3.79	0.90	37.90	30.00	36.08
0	50	0	13.30	0	3.67	0	73.40	73.40
10	50	4.20	16.40	0.58	3.36	58.00	67.20	65.67
20	50	10.33	18.60	0.97	3.14	48.35	62.80	58.67
30	50	17.10	23.00	1.29	2.70	43.00	54.00	49.88
50	50	30.80	29.60	1.92	2.04	38.40	40.80	39.60
100	50	67.20	37.40	3.28	1.26	32.80	25.20	30.27
0	100	0	42.16	0	5.78	0	57.84	57.84
10	100	6.31	42.60	0.37	5.74	36.90	57.40	55.54
20	100	12.45	46.95	0.76	5.31	37.75	53.05	50.50
30	100	19.80	55.70	1.02	4.43	34.00	44.30	41.92
50	100	34.10	67.20	1.59	3.28	31.80	32.80	32.47
100	100	75.30	73.30	2.47	2.67	24.70	26.70	25.70

concentration was changed from 0 to 100 mg/l, at each initial Ni(II) ion concentration of 0, 10, 20, 30, 50 and 100 mg/l. The non-linear adsorption isotherms of Cd(II) ions with Ni(II) ion concentration as the parameter are shown in Fig. 5. It is seen that the equilibrium Cd(II) uptake increases with increasing initial Cd(II) concentration up to 100 mg/l at all Ni(II) ion concentrations. The curvilinear relationship between the amount of Cd(II) adsorbed per unit mass of BFA and the residual Cd(II) concentration at equilibrium suggests that the saturation of BFA-binding sites could occur only at higher concentrations. The equilibrium uptake of Cd(II) decreases with increasing Ni(II) ion concentration. The individual and total adsorption equilibrium uptakes by BFA and the yields of Cd(II) and Ni(II) ions at different Cd(II) concentrations at different initial concentrations of Ni(II) ions are also listed in Table 1. In general, the increase in the initial Ni(II) ion concentration decreases the individual adsorption yields of Cd(II) and the total adsorption yields for each experimental run. The results also show that the equilibrium uptake of Cd(II) ions decreases with increasing initial Ni(II) ion concentration. At 100 mg/l initial Cd(II) ion concentration and, in the absence of Ni(II) ions and in the presence of 100 mg/l Ni(II) ion concentration, the adsorbed Cd(II) ions at equilibrium are found to be 5.18 and 2.47 mg/g, respectively.

In general, a mixture of different adsorbates may exhibit three possible types of behaviour: synergism (the effect of the mixture is greater than that 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 Ni(II) seems to be antagonistic. To analyze the antagonistic adsorption interaction of the two metal ions, the adsorption yields of the 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 54.80% for the total metal concentration of 200 mg/l containing equal (100 mg/l) concentration of Cd(II) and Ni(II) in the mixture $[\mathrm{Ad}_{\mathrm{Tot}}\% = 54.80 = 100 \times [(51.76\ \mathrm{mg/l}\ \ \mathrm{Cd(II)} + 57.84\ \mathrm{mg/l}$ $\mathrm{Ni(II)\ ion})/200\ \mathrm{mg/l\ initial\ total\ concentration}]]$. However, the total experimental adsorption yield was 25.70% for total metal ions concentration of 200 mg/l consisting of 100 mg/l each of Cd(II) and Ni(II) ions [$Ad_{Tot}\% = 25.70 = 100 \times$ [(24.70 mg/l Cd(II) + 26.70 mg/l Ni(II) ion)/200 mg/l initial total concentration]]. This shows that the binary solution exhibited inhibitory (antagonistic) adsorption for each metal, thereby resulting in a lower sorption yield.

The uptake of Ni(II) ions in the absence and presence of Cd(II) ions in the range of 10–100 mg/l concentrations was also studied. Fig. 6 depicts the variation of Ni(II) uptake at equilibrium with increasing initial Ni(II) concentrations (from 0 to 100 mg/l) at a constant initial Cd(II) concentration (10–100 mg/l) at pH_0 6.0. Similar adsorption patterns have been observed both in the single component (Ni(II) ion) and the binary (Cd(II)–Ni(II) ion) systems; Ni(II) ion equilibrium uptake increases with increasing initial Ni(II) ion concentration up to 100 mg/l. Increase in Cd(II) concentration decreases the equilibrium uptake of Ni(II) ion. Table 1 also shows the effect of Cd(II) ions on the equilibrium uptake of Ni(II) ions, both singly and in a mixture, individual Ni(II), individual Cd(II) and total adsorption yields at pH_0 6.0. It is found that the presence of Cd(II) retards the equilibrium uptake of Ni(II) ions from the solution. In the absence of Cd(II) in the solution, the equilibrium Ni(II) uptake is found to be 5.78 mg/g at the initial Ni(II) ion concentration of 100 mg/l. When the concentration of Cd(II) is kept at 100 mg/l in the solution at the same initial Ni(II) ion concentration, the equilibrium Ni(II) uptake decreases to 2.67 mg/g.

4.4. *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 Ni(II) ions onto BFA. The experimental equilibrium adsorption data were obtained by varying the concentrations of Cd(II) or Ni(II) ions with a fixed dosage of BFA (10 g/l).

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 linear regression coefficients, R^2. BFA has a heterogeneous surface for the adsorption of metal ions. Therefore, it is expected that the Freundlich and R–P isotherm equations can better represent the equilibrium sorption data. 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 adsorption data of Cd(II) and Ni(II) ion adsorption on BFA can be represented appropriately by the R–P and the Freundlich models in the studied concentration range.

The single-component Freundlich constants, K_F and n indicate the adsorption capacity and adsorption intensity, respectively. Higher the value of the exponent 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 Ni(II) ions. Since $n < 1$; both the metal ions are favourably adsorbed by BFA at pH_0 6.0. The K_F values indicate the higher uptake of Ni(II) than that of Cd(II) ions by BFA. The value of the R–P constant β between 0 and 1 indicates favourable adsorption. The β values for Ni(II) and Cd(II) ions are found to be about 0.60 and 0.55, respectively. Therefore, both Ni(II) and Cd(II) ions are adsorbed favourably and that adsorption of Ni(II) is favoured in comparison to that of Cd(II) by BFA. Thus, both the isotherm models, viz., Freundlich and R–P, indicate the same conclusion. The values of the Freundlich and Langmuir constants for the adsorption of Cd(II) and Ni(II) onto different adsorbents under different environmental conditions have been reported in the literature. A comparison 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. It is, therefore, necessary to be cautious while using these isotherm parameter values in the design of adsorption systems. Comparison of q_m values shows that the BFA exhibits a reasonable capacity for Cd(II) and Ni(II) adsorption from aqueous solutions. The comparison of the experimental and predicted equilibrium uptakes (q_e) from the single-component Freundlich and R–P models for the individual adsorption of Cd(II) and Ni(II) from the aqueous solution of different concentration onto BFA at pH_0 6.0 are presented in Table 4 along with their MPSD values. The R–P model shows a better fit to the experimental adsorption data than the Freundlich model.

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

Langmuir constants

Adsorbate	K_L (l/mg)	q_m (mg/g)	R^2
Cadmium	0.0899	6.1942	0.9857
Nickel	0.1534	6.4887	0.9852

Freundlich constants

Adsorbate	K_F ((mg/g)/(mg/l)$^{1/n}$)	n	R^2
Cadmium	0.8544	0.4693	0.9995
Nickel	1.2865	0.4016	0.9995

Redlich–Peterson constants

Adsorbate	K_R (l/g)	a_R (l/mg)	β	R^2
Cadmium	10.4449	11.3658	0.5489	0.9997
Nickel	306.786	237.387	0.5997	0.9998

4.5. *Multi-component adsorption models*

The simultaneous adsorption data of Cd(II) and Ni(II) from the binary mixture onto BFA have been fitted to the multi-component isotherm models, viz., non-modified and modified Langmuir models, extended Langmuir and Freundlich models, and the SRS model. The parametric values of all the multi-component 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 Ni(II) are also given in Table 5. The comparisons of the experimental and calculated q_e values of Cd(II) and Ni(II) ions in mixtures are also presented in the parity plots shown in Figs. 7 and 8. Since, most of the data points are

Table 3
Freundlich and Langmuir constants for adsorption of cadmium(II) and nickel(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	–	–	106.452	0.009	[48]
Afsin-Elbistan fly ash	–	–	0.294	179.400	[49]
Seyitomer fly ash	–	–	0.216	11.084	[49]
Fontinalis antipyretica	–	–	29.000	0.130	[50]
Amberlite IR-120 resin	–	–	101.056	0.009	[51]
Baker's yeast cells	3.08	1.450	31.750	0.092	[52]
Akaganeite-type nanocrystals	1.94	0.403	17.100	0.029	[53]
Pelvetia caniculata	13.00	0.357	75.000	0.075	[54]
Corncob	3.72	0.074	5.090	1.230	[55]
Corncob (oxidized 0.6 M CA[a])	26.10	0.192	55.200	0.330	[55]
Corncob (oxidized 1 M NA[b])	13.50	0.081	19.300	0.570	[55]
Bagasse fly ash	0.85	0.469	6.194	0.089	Present work
Nickel					
Pine bark	–	–	6.282	0.022	[56]
Yohimbe bark	–	–	8.806	1.049	[57]
Cork bark	–	–	41.097	0.545	[57]
Steel converter slag	8.1	0.357	–	–	[58]
Afsin-Elbistan fly ash	–	–	0.987	2.092	[59]
Seyitomer fly ash	–	–	1.160	1.839	[59]
Almond husk AC[c]	4.20	0.467	30.769	0.025	[60]
Almond husk AC[c] (SA[d])	0.06	1.202	30.769	0.091	[60]
Baker's yeast	–	–	11.400	0.032	[61]
Grape stalks wastes	–	–	10.673	0.023	[62]
Blank alginate beads	6.11	0.301	25.600	0.099	[39]
Free dead algal cells	4.40	0.227	13.900	0.098	[39]
Immobilized dead algal cells	8.85	0.278	31.300	0.145	[39]
Waste apricot AC[c]	–	–	101.010	1.020	[63]
Amberlite IR-120 resin	–	–	48.083	0.029	[51]
Maple sawdust	0.10	0.680	0.273	0.051	[64]
Bagasse fly ash	1.29	0.402	6.489	0.153	Present work

[a] CA: citric acid.
[b] NA: nitric acid.
[c] AC: activated carbon.
[d] SA: sulphuric acid.

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 nickel(II) onto bagasse fly ash

C_0 (mg/l)	C_e (mg/l)	$q_{e,exp}$ (mg/g)	$q_{e,calc}$ (mg/g)		
			Langmuir	Freundlich	R–P
Cadmium					
10	1.1	0.89	0.56	0.89	0.89
20	3.98	1.6	1.63	1.63	1.65
30	7.46	2.25	2.49	2.19	2.21
50	17.1	3.29	3.75	3.24	3.25
100	48.2	5.18	5.03	5.27	5.23
MPSD			23.89	2.39	2.19
Nickel					
10	0.48	0.95	0.45	0.96	0.96
20	2.12	1.79	1.59	1.74	1.74
30	5.41	2.46	2.94	2.53	2.54
50	13.30	3.67	4.35	3.64	3.64
100	42.16	5.78	5.62	5.78	5.78
MPSD			35.07	2.40	2.39

distributed around the 45° line, this indicates that all the multi-component isotherm models could represent the experimental adsorption data for the binary systems with varying degree of fit.

The multi-component non-modified Langmuir model shows a poor fit to the experimental data (MPSD = 95.76). The values of the modified Langmuir coefficient (η) were much lower than 1.0 indicating that the non-modified multi-component Langmuir model related to the individual isotherm parameters could not be used to predict the binary-system adsorption. The use of the interaction term, η, improved the fit of the modified Langmuir model only marginally. The extended Langmuir and the SRS models fitted to the binary adsorption data of Cd(II) and Ni(II) onto BFA reasonably well. However, the extended Freundlich model best-fitted the experimental data with the lowest MPSD value of 13.65 in comparison to other models. This is expected as BFA has heterogeneous surface and the adsorption of the single metal ions have also been well represented by the Freundlich isotherm. It is evident that the modification of the Freundlich equation as given by Eqs. (9) and (10) takes into account the interactive effects of individual metal adsorbate

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

Non-modified Langmuir model	
MPSD	95.763

Modified Langmuir model		Extended Langmuir model	
Adsorbate	η_i	K_i	$q_{\max}$
Cadmium	0.672	0.102	4.528
Nickel	0.990	0.109	
MPSD	80.60	28.81	

Extended Freundlich model

Adsorbate	x_i	y_i	z_i
Cadmium	0.602	0.606	0.795
Nickel	0.768	0.363	1.1462
MPSD	13.65		

SRS model

Adsorbate	a_{12}	a_{21}
Cadmium	2.917	–
Nickel	–	3.015
MPSD	26.83	

ions between and among themselves and the adsorbent reasonably well. Therefore, the binary adsorption of Cd(II) and Ni(II) ions by BFA can be represented satisfactorily and adequately by the modified Freundlich isotherm Eqs. (9) and (10). A three-dimensional graphical representation of the sorption isotherm plot for the binary metal adsorption system is given in Fig. 9. In this plot, the experimental data points are shown along with the predicted isotherms using the extended Freundlich isotherm Eqs. (9) and (10). As can be seen, the predictions are found to be satisfactory.

4.6. Desorption study and disposal of BFA

In the wastewater treatment systems using adsorption process, the regeneration of the adsorbent and/or disposal of the adsorbate loaded adsorbent (or spent adsorbent) are very important. It has been reported that the sorption process of trace metals

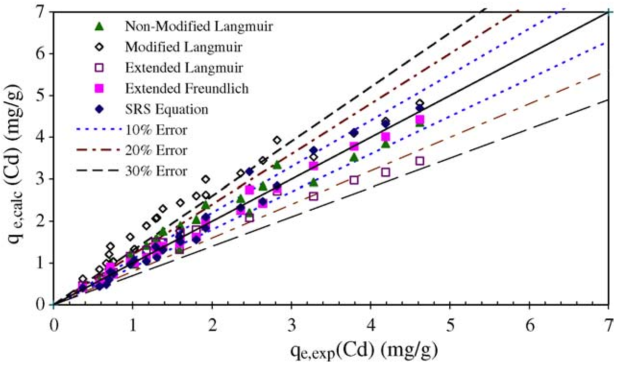

Fig. 7. Comparison of the experimental and calculated q_e values of cadmium(II) ions in a binary mixture of cadmium(II) and nickel(II) ions.

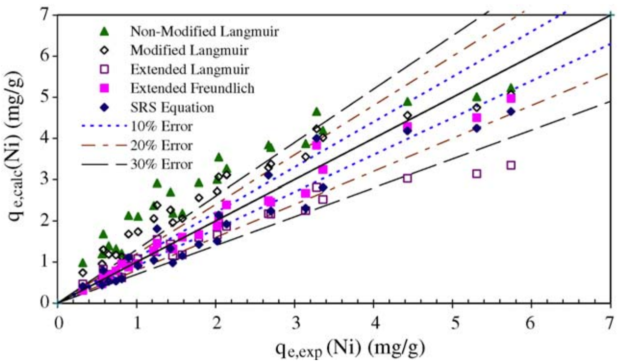

Fig. 8. Comparison of the experimental and calculated q_e values of nickel(II) ions in a binary mixture of cadmium(II) and nickel(II) ions.

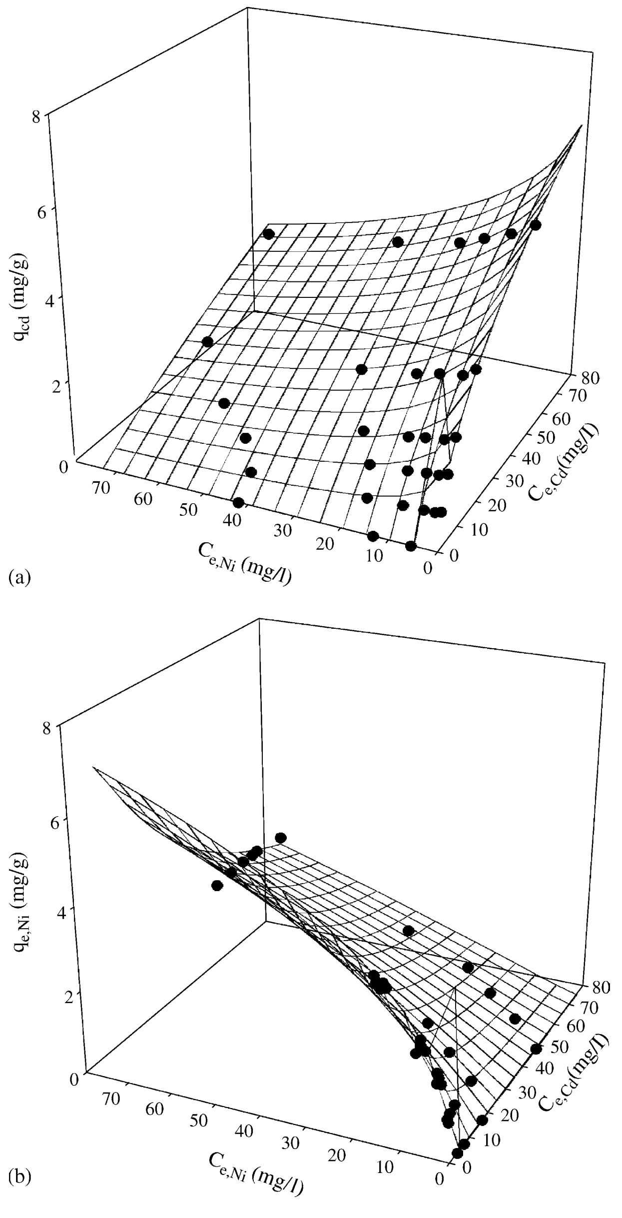

Fig. 9. Binary adsorption isotherms cadmium(II)–nickel(II). The surfaces are predicted by the extended Freundlich model and the symbols are experimental data. (a) Cadmium(II) uptake and (b) nickel(II) uptake.

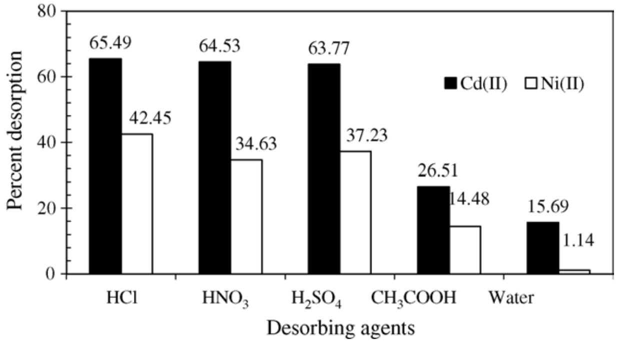

Fig. 10. Desorption efficiencies of metal ions from BFA by various desorbing agents. $T = 30\,°C$, $t = 5$ h, C_0 (desorbing agents) = 0.1N, $m = 10$ g/l.

is not completely reversible. Several explanations have been proposed for such an observation, including diffusion of trace metals within oxide particles or into micropores [42], precipitation [43], incorporation of metals into oxides [44] and readsorption [45].

For the desorption experiments, several solvents (acids, bases and water) have been used. Batch desorption experiments were carried out and the desorption efficiencies are compared in Fig. 10. The use of deionized water resulted in only a limited amount of metal ion desorption (<16%). Acetic acid showed the maximum desorption efficiency of 26.5% for Cd(II) and 14.5% for Ni(II). On the other hand, mineral acids, HCl, H_2SO_4 and HNO_3 showed similar efficiencies with higher recovery efficiencies (≈65%) for Cd(II). However, for Ni(II), HCl proved to be the best. Hydrogen ions released from the acids replace metal cations on the BFA. For all the eluents, the desorption of Cd(II) is greater than that for Ni(II) from BFA.

BFA has a heating value of about 4.6 MJ/kg [46]. It can be utilized for making blended fuel briquettes which could be used as a fuel in the furnaces. The bottom ash obtained after its combustion can be blended with the cementitious mixtures. Setting and leaching tests on the cementitious mixtures have shown that the bottom ash can be incorporated into the cementitious matrices to a great extent (75 wt.% of total solid) without the risks of an unacceptable delay of cement setting and an excessive heavy metals leachability from solidified products [47]. Further studies on the disposal of metal loaded BFA is in progress in our laboratory.

5. Conclusion

The present study shows that the bagasse fly ash is an effective adsorbent for the removal of Cd(II) and Ni(II) metal ions from aqueous solution. The most critical parameter for the process of heavy metal uptake by adsorbents is the pH_0 of the adsorption medium. Maximum sorption for both Cd(II) and Ni(II) metals ions was found to occur at pH_0 6.0. The pH of the system, however, increases during the sorption process and reaches to basic pH levels (<8.4). The adsorptive uptake of metal ions was very fast during the initial sorption period of about 20 min. Freundlich and Redlich–Peterson isotherms show very good fit with the experimental adsorption equilibrium data for single metal ions. In the binary metal mixtures, the affinity of the BFA for Ni(II) ions was marginally greater than that for Cd(II), for both the single and binary metal solutions under the same experimental conditions. The net interactive effect of Cd(II) and Ni(II) ions on the adsorption of Cd(II) ions by BFA was found to be antagonistic. The simultaneous adsorption phenomena of Cd(II) and Ni(II) ions on the BFA can be satisfactorily and adequately represented by the extended Freundlich and the SRS models. Based on Marquardt's percent standard deviation error function, the extended Freundlich isotherm model showed 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 partial elution of the metal ions. Hydrochloric acid was the best eluent showing about 65% elution of Cd(II) and about 42% of Ni(II). 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. The leachability of metal ions from the blocks to aqueous solutions is, however, still under investigation. Finally, it may be concluded that BFA may be used for the individual and simultaneous removal of Cd(II) and Ni(II) ions from metal-containing effluents.

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