Mono- and multi-component biosorption of lead(II), cadmium(II), copper(II) and nickel(II) ions onto coco-peat biomass

K. Vijayaraghavan¹b, S. Rangabhashiyam¹b, T. Ashokkumar¹a, and Jesu Arockiarajc

¹Department of Chemical Engineering, Indian Institute of Technology Madras, Chennai, India; ²Department of Physical and Chemical Foundations of Process Engineering, Max Planck Institute for Dynamics of Complex Technical Systems, Magdeburg, Germany; ³Division of Fisheries Biotechnology & Molecular Biology, Department of Biotechnology, Faculty of Science and Humanities, SRM University, Kattankulathur, Chennai, Tamil Nadu, India

ABSTRACT
The potential of using coco-peat biomass (CPB) has been assessed for the removal of Pb(II), Cd(II), Cu(II) and Ni(II) ions from single and quaternary solutions. According to Langmuir isotherm, the maximum biosorption capacity of CPB was 0.484, 0.151, 0.383 and 0.181 mmol/g for Pb(II), Cd(II), Cu(II) and Ni(II) ions, respectively. Scanning electron microscopy along with energy-dispersive X-ray spectroscopy and Fourier-transform IR spectroscopy confirmed changes in the biosorbent functionality after metal sorption. Through quaternary isotherm experiments, 16.1%, 48.2%, 32.3% and 46.5% decrease in experimental uptakes were observed for Pb(II), Cd(II), Cu(II) and Ni(II), respectively, in the presence of other metal ions.

Introduction
Heavy metal pollution is a major concern nowadays, due to the rapid industrialization and increasing wastewater discharge. Heavy metals are released into the aquatic environment through several industrial activities, such as metallurgy, iron and steel, mining, electroplating, electrolysis, electro-osmosis, metal finishing, battery manufacture, petroleum refining, pesticides, pigment manufacture, tanneries, photography, etc.¹,² Heavy metals are nondegradable substances, and their persistence in the environment probably accumulates in biological systems through food chain and thus may pose major hazardous effects on human health.³ Heavy metal toxicity leads to various diseased conditions such as lung cancer, chronic bronchitis, gastrointestinal distress, dermatitis, nausea, lethargy, anaemia and damage to blood composition, lungs, kidneys, liver, central nervous system and other important organs.⁴ Hence, reduction of heavy metals from industrial waste streams to acceptable levels is highly desirable.

The conventional methods for the removal of heavy metals including chemical precipitation, ion exchange, coagulation, membrane filtration, reverse osmosis, solvent extraction and electrolysis are found to be unsatisfactory. Because these methods involve high capital, deficient of eco-friendliness and ineffective in the heavy metal concentration of 1–100 mg/L.⁵,⁶ Therefore, an alternative treatment technology for the removal of heavy metals is needed. Biosorption is an innovative process, which utilizes dead biomass for the removal of heavy metals. Biosorption using lignocellulosic biomass holds the merits of higher biosorption capacity, more economical, vast availability and repeated use of the biomass.⁷ Various agricultural waste biomass acts as a significant tool for the removal of heavy metals from the wastewater.⁸ Coco-peat is a lignocellulosic light fluffy biomass obtained during the fibre separation from the ripened coconut husk.⁹ In recent years, coco-peat is widely used as soil-less medium for plants in green roofs¹⁰ and biofilters.¹¹ Very few authors successfully employed coco-peat for the removal of heavy metals from mono-metal solutions.⁹,¹² However, industrial effluents usually comprised of multicomponent pollutants; therefore, the assessment over the metal biosorption in single-component system alone may not be adequate.¹³

To the best of our knowledge, coco-peat biomass (CPB) has not been previously investigated for the biosorption of metal ions in quaternary system.¹²,¹⁴ In the present work the biosorption of Pb(II), Cd(II), Cu(II) and Ni(II) ions by coco-peat was studied in single and quaternary solutions in order to understand the interactions between the metal ions during biosorption. The effect of parameters such as the solution pH, contact time and initial metal ions concentration on the
biosorption capacity of coco-peat were evaluated. Various equilibrium and kinetic models were utilized to describe biosorption of metal ions onto coco-peat biomass.

**Materials and methods**

**Preparation of biosorbent**

CPB was obtained from a local nursery. The CPB was washed thoroughly with deionized water and oven dried at 60°C for 48 h. The biomass was initially grounded and subsequently sieved to obtain average particle sizes in the range of 0.75 mm. The prepared CPB was then stored in a vacuum desiccator for further use without any pretreatment. The bulk density, water-holding capacity and air-filled porosity of CPB were determined according to the Australian Standard Methods for potting mixes.[15] The cation exchange capacity (CEC) was quantified by ammonium acetate method according to the procedure proposed by Ming and Dixon.[16] Scanning electron microscopy (Hitachi S4800, Japan) along with energy-dispersive X-ray spectroscopy characterization was also performed to obtain direct observation of the surface texture and morphology of the CPB. The mechanism of metal removal by CPB and the involvement of binding sites were evaluated using a Bruker-ATR IR (ACPHA) Fourier Transform IR spectrophotometer (Germany). The samples were prepared in the form of pellets using KBr.

**Preparation of synthetic solutions**

The stock solutions of Pb(II), Cd(II), Cu(II) and Ni(II) ions were prepared in deionized water using the nitrate salts of heavy metals including Pb(NO₃)₂, Cd(NO₃)₂·4H₂O, Cu(NO₃)₂·3H₂O and Ni(NO₃)₂·6H₂O, respectively. All working solutions of different concentrations were obtained by diluting the stock solutions. The pH of the solution was adjusted to the desired value by using 0.1 M HCl or 0.1 M NaOH. All the chemicals used in this study were of analytical grade and were purchased from Sigma Aldrich (India).

**Biosorption experiment**

A batch mode operation was used to study the removal of heavy metal ions from aqueous solution. Adsorption behaviour of each metal ion was studied by varying solution pH, contact time and initial metal concentration. The biosorption studies were performed in a 250 mL Erlenmeyer flask with 0.2 g of CPB in 100 mL of known concentration of the metal solution. The solution was agitated on a thermostated shaking incubator at 160 rpm and 32 ± 1°C for 8 h. After sufficient contact time, the samples were filtered using 0.45-µm-pore-size membrane syringe filter and analysed for the residual metal ion concentration using inductively coupled plasma-optical emission spectrometry (ICP-OES) (Perkin Elmer Optima 5300 DV). Similar to the above-mentioned single-component biosorption study, the multicomponent biosorption study was performed using equal concentrations of Pb(II), Cd (II), Cu(II) and Ni(II) ions (mmol/L) with 0.2 g of CPB.

**Biosorption isotherm**

The equilibrium sorption isotherm examines the relationship between adsorbate and adsorbent at the equilibrium condition. In the present work, isotherm models like Langmuir, Freundlich and Redlich–Peterson were used to analyse the equilibrium data of single-component biosorption study.

**Langmuir model**

The Langmuir isotherm is based on the assumption of monolayer coverage on homogenous biosorbent surface without any interaction between adsorbed ions.[17] The Langmuir isotherm model is used to calculate the maximum biosorption capacity of the biosorbent. The Langmuir isotherm model can be expressed by the following equation:

$$Q = \frac{Q_0 b_L C_e}{1 + b_L C_e}$$

where $Q$ represents the amount of metal ions biosorbed per unit mass of biosorbent (mmol/g), $C_e$ is the equilibrium concentration of metal ion (mmol/L), $Q_0$ is the monolayer coverage capacity (mmol/g) and $b_L$ is the Langmuir isotherm constant (L/mmol).

**Freundlich model**

The Freundlich isotherm model[18] represents an empirical equation. It describes that the biosorption occurs on a heterogeneous surface with interaction between the biosorbed molecules. The Freundlich isotherm model is commonly presented as

$$Q = K_F C_e^{1/n_F}$$

where $K_F$ indicates the Freundlich isotherm constant (mmol/g) (L/mmol)$^{1/n_F}$ and $n_F$ is the Freundlich exponent.

**Redlich–Peterson model**

The Redlich–Peterson isotherm model[19] is an empirical isotherm incorporating three parameters. It includes the features of both Langmuir and Freundlich
isotherms and describes the mechanism of biosorption as hybrid. The Redlich–Peterson isotherm expression can be represented as follows:

\[
Q = \frac{K_{RP}C_e}{1 + a_{RP}C_e^{\beta_{RP}}} \quad (3)
\]

where \(K_{RP}\) indicates the Redlich–Peterson model isotherm constant (L/g), \(a_{RP}\) represent the Redlich–Peterson model constant (L/mmol)\(^{\beta_{RP}}\) and \(\beta_{RP}\) is the Redlich–Peterson model exponent.

**Biosorption kinetics**

Biosorption kinetics is vital to design, model and to control the process. In this study, kinetic models like the pseudo-first-order,\(^{20}\) pseudo-second-order,\(^{21}\) and Elovich\(^{22}\) models were applied to the experimental data.

**Pseudo-first-order model**

The pseudo-first-order rate equation of Lagergren is generally presented as follows:

\[
Q_t = Q_e(1 - \exp(-k_1t)) \quad (4)
\]

where \(Q_e\) and \(Q_t\) are the amounts of metal ion biosorbed (mmol/g) at equilibrium and at any time \(t\), respectively and \(k_1\) (1/min) is the pseudo-first-order rate constant.

**Pseudo-second-order model**

The pseudo-second-order kinetic model is expressed as follows:

\[
Q_t = \frac{Q^2_k k_2 t}{1 + Q^2_k k_2 t} \quad (5)
\]

where \(k_2\) (g/mmol min) represents the pseudo-second-order rate constant.

**Elovich model**

The Elovich kinetic model can also be used to describe the biosorption. The equation is represented below:

\[
Q_t = \frac{1}{b} \ln(1 + abt) \quad (6)
\]

where \(a\) is the initial biosorption rate (mmol/g min), and \(b\) is the desorption constant (g/mmol).

The isotherms and kinetics were calculated by applying nonlinear regression using the Sigma Plot (version 4.0, SPSS, USA) software. The coefficient of determination and average percentage error were employed to ascertain the fit of all biosorption isotherm and kinetics models with the experimental data.

**Results and discussion**

**Characterization of coco-peat**

On analysis, it was found that CPB has low bulk density (115 kg/m\(^3\)), and high CEC (51.2 meq/100 g), water-holding capacity (46.3%) and air-filled porosity (10.7%).\(^{23}\) The high CEC value observed for CPB implies that the material has the potential to act as sorbent for metal cations.

The scanning electron microscopy was used to evaluate the surface morphology of CPB samples as shown in Fig. 1. According to Fig. 1a, CPB has complex, uneven and rough morphology. In EDX analysis, strong peaks of Si, C and O were observed (Fig. 2a).

The FTIR spectrum of raw CPB is presented in Fig. 3 and the spectrum displayed a number of absorption peaks, which indicates the complex nature of coco-peat. The presence of broad band at 3412 cm\(^{-1}\) indicates the stretch vibration of bonded hydroxyl groups on CPB sample. The broad absorption peak at 2925 cm\(^{-1}\) denotes alkyl stretch vibration of –CH\(_3\). On the other hand, peak at 2095 cm\(^{-1}\) corresponds to C≡C stretching vibrations.\(^{24}\) The strong absorption peak at 1624 cm\(^{-1}\) attributes the presence of conjugate

Figure 1. SEM images of (a) CPB and (b) multi-metal-loaded CPB.
C–C bond of diene. The vibration at 1382 cm$^{-1}$ is due to a possible C-O-H bend. The existence of C–O of carboxylic acid groups gave rise to the peak at 1264 cm$^{-1}$. The peak shown at 1042 cm$^{-1}$ is associated with the strong and broad band of C–O of primary alcohol and medium vibration of primary amine (–NH$_2$) in the structure. The stretched adsorption peak at 542 cm$^{-1}$ could be assigned to the presence of alkyl halide (C–X) and disulphide groups.$^{[25]}$

**Effect of solution pH on metal ions biosorption**

The influence of solution pH on the metal ions uptake by CPB was studied at the pH range from 2.0 to 5.0 and at a fixed initial metal ion concentration of 1.5 mmol/L. The results (Fig. 4) of the metal ions uptake by the CPB at different solution pH values provide information about the favourable range of solution pH for the biosorption process. The biosorption capacity of CPB towards Pb(II), Cd(II), Cu(II) and Ni(II) ions removal at pH 4 was observed as 0.440, 0.133, 0.335 and 0.154 mmol/g, respectively. On the other hand, at the solution pH of 2, uptake was determined as 0.086, 0.027, 0.101 and 0.043 mmol/g, respectively. This could be explained by the fact that the protonation of the CPB surface consequently leads to the competition between protons and metal ions for the binding sites. Also, the metal speciation is highly dependent on solution pH. The free Pb(II), Cd(II), Cu(II) and Ni(II) ions were the predominant species at the solution pH of below 6.0.$^{[26]}$ This study was confined in the acidic pH range and not in the basic pH, because the metal ion precipitation may occur at the solution pH of above 5.0.$^{[27]}$ The biosorption capacity of CPB for all the metal ions was observed higher at the solution pH of 4 and therefore it was regarded as optimum pH for the subsequent studies.

Figure 2. Energy-dispersive X-ray analyses of (a) CPB and (b) multi-metal-loaded CPB.

Figure 3. FTIR spectra of CPB and multi-metal-loaded CPB samples.

Figure 4. Effect of solution pH on biosorption of Pb(II), Cd(II), Cu(II) and Ni(II) ions onto CPB.
**Biosorption kinetics**

Batch biosorption kinetic experiments were carried out to explore the rate of biosorption by CPB at different metal ion concentrations. Biosorption kinetics data are important in understanding the dynamics of the process and thereby help in selecting the optimal operating conditions. It is also useful in analysing the mechanism and rate-controlling step of the biosorption process.

The kinetics data of biosorption capacity versus time was plotted to get the biosorption rate curves for the Pb(II), Cd(II), Cu(II) and Ni(II) ions, as shown in Fig. 5. The rate of metal ions uptake by CPB was rapid up to 30 min and subsequently attained equilibrium within 120 min. The biosorption capacity of CPB towards the metal ions removal did not change significantly after attaining the equilibrium time. The biosorption rate is controlled by several factors like the structural properties of CPB and metal ions, CPB dosage and initial concentration of metal ions. In general, sorption of metal ions onto the sorbent occurs through two phases. The first phase is usually rapid, whereas the second phase is relatively slow and this usually leads to equilibrium. The fast sorption rate during first phase is due to the presence of large number of exchangeable binding sites. With progression of time, the binding sites get saturated and eventually the sorption rate reduces. Analysing Fig. 5, it can be inferred that the rate and extent of sorption was observed to be high for Pb(II) ions. The experimental values of Qe for Pb(II), Cd(II), Cu(II) and Ni(II) were found as 0.400, 0.125, 0.294 and 0.152 mmol/g, respectively.

In the present study the biosorption kinetics data were described using kinetic models such as pseudo-first-order, pseudo-second-order and Elovich models. Table 1 represents the estimated kinetic parameters for each model along with error functions. The pseudo-first-order kinetic model showed a good fitting for biosorption of metal ions with high $R^2$ (>0.991) and low % error (<1.86) values. It was observed that the calculated values of $Q_e$ using pseudo-first-order kinetic model were very close to the experiment values and therefore implies better fitness of pseudo-first-order kinetic model to the present data. It was evident from Table 1 that $R^2$ and % error values of pseudo-second-order kinetic model were slightly inferior to that of pseudo-first-order model. Also, the pseudo-second-order model over-predicted equilibrium values (Table 1). The Elovich kinetic model parameters are also presented in Table 1. Compared to the pseudo-first-order and pseudo-second-order kinetic models, the $R^2$ values were lower and % error values were higher. The study over the three kinetic models revealed that the Elovich was the least fitted, whereas pseudo-first-order model was the best-fitted model for the experimental kinetics data.

**Biosorption isotherms**

Biosorption isotherms are important to optimize the usage of biosorbent, design of biosorption system and to establish the suitable correlation for the equilibrium curve. The biosorption isotherms were evaluated by varying initial metal ion concentration at fixed solution pH. The biosorption isotherms of Pb(II), Cd(II), Cu(II) and Ni(II) using CPB are illustrated in Fig. 6. The isotherm curves obtained

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**Figure 5.** Biosorption kinetics of Pb(II), Cd(II), Cu(II) and Ni(II) onto CPB.

**Table 1.** Biosorption isotherm and kinetic model constants obtained during the removal of Pb(II), Cd(II), Cu(II) and Ni(II) from single-solute aqueous solution by CPB.

<table>
<thead>
<tr>
<th>Model</th>
<th>Pb(II)</th>
<th>Cd(II)</th>
<th>Cu(II)</th>
<th>Ni(II)</th>
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<tr>
<td>Langmuir</td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>$Q_e$ (mmol/g)</td>
<td>0.484</td>
<td>0.151</td>
<td>0.383</td>
<td>0.181</td>
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<tr>
<td>$b_1$ (L/mmol)</td>
<td>18.3</td>
<td>6.99</td>
<td>7.88</td>
<td>7.76</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.997</td>
<td>1.999</td>
<td>0.991</td>
<td>0.993</td>
</tr>
<tr>
<td>% error</td>
<td>4.37</td>
<td>3.47</td>
<td>4.45</td>
<td></td>
</tr>
<tr>
<td>% error</td>
<td>0.956</td>
<td>0.938</td>
<td>0.965</td>
<td></td>
</tr>
<tr>
<td>$n_L$</td>
<td>6.74</td>
<td>2.41</td>
<td>5.88</td>
<td>1.95</td>
</tr>
<tr>
<td>$K_L$ (L/mmol)</td>
<td>0.896</td>
<td>2.06</td>
<td>1.06</td>
<td></td>
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<tr>
<td>$k_1$ (min⁻¹)</td>
<td>0.899</td>
<td>2.12</td>
<td>5.88</td>
<td></td>
</tr>
<tr>
<td>$k_2$ (mmol/min)</td>
<td>9.11</td>
<td>1.29</td>
<td>5.88</td>
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<tr>
<td>$R^2$</td>
<td>0.995</td>
<td>0.998</td>
<td>0.995</td>
<td>0.997</td>
</tr>
<tr>
<td>% error</td>
<td>4.37</td>
<td>3.47</td>
<td>4.45</td>
<td></td>
</tr>
<tr>
<td>% error</td>
<td>0.956</td>
<td>0.938</td>
<td>0.965</td>
<td></td>
</tr>
<tr>
<td>$n_F$</td>
<td>6.24</td>
<td>4.14</td>
<td>2.41</td>
<td>1.06</td>
</tr>
<tr>
<td>$K_F$ (L/mmol)²</td>
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<td>5.76</td>
<td>6.20</td>
<td>5.57</td>
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<tr>
<td>$k_F$ (min⁻¹)</td>
<td>1.12</td>
<td>1.06</td>
<td>1.13</td>
<td>1.12</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.995</td>
<td>0.998</td>
<td>0.995</td>
<td>0.997</td>
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<tr>
<td>% error</td>
<td>4.37</td>
<td>3.47</td>
<td>4.45</td>
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<tr>
<td>% error</td>
<td>0.956</td>
<td>0.938</td>
<td>0.965</td>
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<tr>
<td>Pseudo-first</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>order</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Q_e$ (mmol/g)</td>
<td>0.398</td>
<td>0.124</td>
<td>0.292</td>
<td>0.152</td>
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<tr>
<td>$k_1$ (min⁻¹)</td>
<td>0.084</td>
<td>0.072</td>
<td>0.082</td>
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<tr>
<td>$R^2$</td>
<td>0.996</td>
<td>0.992</td>
<td>0.996</td>
<td>0.995</td>
</tr>
<tr>
<td>% error</td>
<td>4.37</td>
<td>3.47</td>
<td>4.45</td>
<td></td>
</tr>
<tr>
<td>% error</td>
<td>0.956</td>
<td>0.938</td>
<td>0.965</td>
<td></td>
</tr>
<tr>
<td>Pseudo-second</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>order</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Q_e$ (mmol/g)</td>
<td>0.431</td>
<td>0.136</td>
<td>0.317</td>
<td>0.166</td>
</tr>
<tr>
<td>$k_2$ (g/mmol)</td>
<td>0.293</td>
<td>0.751</td>
<td>0.386</td>
<td>0.451</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.969</td>
<td>0.966</td>
<td>0.969</td>
<td>0.977</td>
</tr>
<tr>
<td>% error</td>
<td>2.20</td>
<td>3.89</td>
<td>2.84</td>
<td>2.44</td>
</tr>
<tr>
<td>% error</td>
<td>0.600</td>
<td>0.086</td>
<td>0.381</td>
<td>0.050</td>
</tr>
<tr>
<td>Elovich</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>$a$ (mmol/g/min)</td>
<td>18.4</td>
<td>52.1</td>
<td>24.5</td>
<td>38.1</td>
</tr>
<tr>
<td>$b$ (g/mmol)</td>
<td>0.868</td>
<td>0.865</td>
<td>0.865</td>
<td>0.892</td>
</tr>
<tr>
<td>$R^2$</td>
<td>4.46</td>
<td>6.91</td>
<td>5.38</td>
<td>5.45</td>
</tr>
<tr>
<td>% error</td>
<td>4.46</td>
<td>6.91</td>
<td>5.38</td>
<td>5.45</td>
</tr>
</tbody>
</table>
for all metal ions were concave-shaped and favourable. To be precise, the isotherm obtained for Pb(II) was H-shaped, whereas L-shaped isotherms were obtained for Cd(II), Cu(II) and Ni(II) ions. The L-shaped isotherm infers that the ratio between the solute concentration remaining in solution and those adsorbed onto the sorbent decreases when the solute concentration increases.\(^\text{[29]}\) The H-shaped isotherm is a special case of the L-shaped isotherm,\(^\text{[30]}\) where the initial slope is very high. In the present study, the equilibrium isotherm data observed for metal ions were described using isotherm models such as the Langmuir, Freundlich, and Redlich–Peterson.

Table 1 shows the values of the Langmuir isotherm parameters such as the monolayer metal biosorption capacity of the CPB and the Langmuir isotherm constant. The Langmuir model described the biosorption data with high \(R^2\) values and low % error values. The order of the monolayer coverage capacity of the CPB towards four metal ions was in the following sequence of Pb(II) > Cu(II) > Ni(II) > Cd(II). Table 2 compares the maximum adsorption capacity (\(Q_0\)) of CPB for Pb(II), Cd(II), Cu(II) and Ni(II) ions obtained in the present study with other sorbents reported in the literature. From Table 2, it can be inferred that CPB showed relatively high metal sorption capacities compared to most of the other sorbents. The Freundlich isotherm parameters are listed in Table 1. The obtained \(n_f\) values of CPB for all the metal ions were greater than 1.0, indicating the favourable biosorption process. The low \(R^2\) values and high % error values specify that the biosorption equilibrium data of the present study were not fitted well with the Freundlich isotherm model. In addition to the two-parameter isotherm models, a three-parameter isotherm model (Redlich–Peterson) was used to analyse the biosorption equilibrium data. The Redlich–Peterson isotherm equation includes the features of the previously discussed Langmuir and Freundlich isotherm models. The values of Redlich–Peterson model exponent, \(\beta_{RP}\) (Table 1), were near to unity and this indicates that the biosorption process was close to the Langmuir isotherm than the Henry’s law. The higher \(R^2\) values (>0.994) and lower % error values (<2.02) for Redlich–Peterson isotherm model suggest that it was the best-fitted model to describe biosorption of Pb(II), Cu(II), Ni(II) and Cd(II) onto CPB.

**Multicomponent biosorption isotherm**

Next, experiments were performed to understand the effect of multicomponent metal ions on the biosorption capacity of CPB. The examination of the multicomponent biosorption is crucial, since the industrial wastewater is often associated with various metal ions which may significantly affect the biosorption of targeted metal ion. Hence, in the present investigation, the effect of quaternary mixture of Pb(II), Cd(II), Cu(II) and Ni(II) on the biosorption potential of CPB was studied and quaternary biosorption isotherms were evaluated (Fig. 7). Comparing the results of quaternary biosorption with the mono-metal biosorption, there was a considerable decrease in Pb(II) uptake by CPB. Whereas moderate to severe decrease in the uptakes of Cd(II), Cu(II) and Ni(II) by CPB was observed in quaternary mixture. For instance, while comparing mono- and quaternary systems, 16.1%, 48.2%, 32.3% and 46.5% decrease in experimental uptakes was observed for Pb(II), Cd(II), Cu(II) and Ni(II) in the presence of other metal ions. The decrease of the biosorption capacity in the quaternary system may be attributed to the repulsive effect of the individual metal ions in the quaternary system and competition of the metal ions for the limited binding sites over CPB.\(^\text{[31]}\)

The SEM image of multi-metal-loaded CPB sample is presented in Fig. 1b. The surface of the metal-loaded CPB appeared relatively smooth compared to raw CPB sample.
Figure 1a. EDX data confirmed the biosorption of metal ions onto the surface of CPB as peaks of Cu, Cd, Ni and Pb were observed in EDX spectrum of multi-metal-loaded CPB (Fig. 2b). The FTIR spectrum of multi-metal-loaded CPB sample is shown in Fig. 3. After biosorption, all peaks appearing in the raw CPB sample (Fig. 3) shifted to a new wavelength, which is an indication of the involvement of the functional groups in the adsorption process. For instance, peaks at 3412, 2925, 2095, 1624, 1382, 1264, 1042 and 542 cm$^{-1}$ appearing in raw CPB sample shifted to 3417, 2924, 2091, 1627, 1383, 1266, 1036 and 603 cm$^{-1}$ in metal-loaded CPB sample.

The Sheindorf–Rebhun–Sheintuch (SRS)\cite{32} model has proposed an equation to describe the experimental data of the multicomponent system. The SRS isotherm can be presented using the following equation:

$$Q_{eq,i} = K_{F,i}C_{eq,i} \left[ \sum_{j=1}^{n} \theta_{ij}C_{eq,j} \right]^{1/n_i - 1} \tag{7}$$

where $Q_{eq,i}$ represents the biosorption uptake of metal ion $i$, $K_{F,i}$ indicates the single-component Freundlich constant for metal ion $i$, $n_i$ specifies the Freundlich exponent for metal ion $i$, $\theta_{ij}$ is the competitive coefficient and $C_{eq,i}$ is the equilibrium concentration of metal ion $i$. The SRS model was able to describe multicomponent isotherm data with high $R^2$ and low % error values as presented in Table 3. The competitive coefficient was recorded lowest for Pb, which implies the competition exhibited by other metal ions during Pb sorption was lowest. On the other hand, $\theta_{ij}$ was recorded highest for Cd, which confirms the superior competition of other ions over Cd and this inference coincides with the experimental data of both single and quaternary isotherm data.

Table 3. Competitive coefficients obtained from SRS equation during multicomponent biosorption of Pb(II), Cd(II), Cu(II) and Ni(II) by CPB.

<table>
<thead>
<tr>
<th></th>
<th>$\theta_{Cu,Ni}$</th>
<th>$\theta_{Cu,Pb}$</th>
<th>$\theta_{Cu,Cd}$</th>
<th>$\theta_{Ni,Cu}$</th>
<th>$\theta_{Ni,Pb}$</th>
<th>$\theta_{Ni,Cd}$</th>
<th>$R^2$</th>
<th>% error</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\theta_{Cu,Ni}$</td>
<td>0.18</td>
<td>0.24</td>
<td>0.15</td>
<td>0.74</td>
<td>1.01</td>
<td>0.64</td>
<td>0.925</td>
<td>3.64</td>
</tr>
<tr>
<td>$\theta_{Cu,Pb}$</td>
<td>0.24</td>
<td>0.15</td>
<td>0.925</td>
<td>0.74</td>
<td>1.01</td>
<td>0.64</td>
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<td>0.925</td>
<td>3.64</td>
</tr>
<tr>
<td>$\theta_{Ni,Cu}$</td>
<td>0.74</td>
<td>1.01</td>
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<td>0.925</td>
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<td>0.925</td>
<td>0.64</td>
<td>0.925</td>
<td>3.64</td>
</tr>
<tr>
<td>$\theta_{Ni,Cd}$</td>
<td>0.64</td>
<td>0.925</td>
<td>0.64</td>
<td>0.925</td>
<td>0.64</td>
<td>0.925</td>
<td>0.925</td>
<td>3.64</td>
</tr>
</tbody>
</table>

Conclusions

In the present investigation the potential of CPB towards the removal of Pb(II), Cd(II), Cu(II) and Ni(II) ions from single and quaternary solutions in batch mode operation was evaluated. The biosorption capacity of CPB towards the four metal ions was analysed with respect to solution pH, initial metal ion concentration and contact time. The maximum uptake of metal ions by CPB was observed at the solution pH of 4.0. The equilibrium data were analysed by the Langmuir, Freundlich and Redlich–Peterson isotherm models. In comparison of all the three models, the Redlich–Peterson isotherm model best fitted the equilibrium data. The kinetic equilibrium data of the biosorption process were adequately fitted by the pseudo-first-order kinetic model. The multicomponent SRS equation effectively explained the quaternary isotherm data with high $R^2$ and low % error values. The analysis over the results of SRS model depicted that CPB preferentially biosorbed Pb(II) over Cd(II), Cu(II) and Ni(II) ions. Thus, the present study has demonstrated that the raw CPB could be used as an economical and practical biosorbent for the removal of Pb (II), Cd(II), Cu(II) and Ni(II) ions from single- and multi-component systems.

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References


