Kinetic and equilibrium modeling of biosorption of nickel (II) and cadmium (II) on brewery sludge

Rajeswari M. Kulkarni, K. Vidya Shetty and G. Srinikethan

ABSTRACT

In the current study, utilization of industrial waste brewery sludge for the biosorption of nickel (II) and cadmium (II) has been explored. The suitable conditions for the effective removal of Ni (II) and Cd (II) from aqueous solutions were examined. The kinetic evaluation showed that the biosorption process using the sludge followed pseudo-second order kinetics. In the presence of a metal co-ion, competitive and preferential biosorption was observed. The Langmuir model and Freundlich model were able to describe the sorption equilibrium for biosorption of Ni (II) and Cd (II) ions in single and dual metal systems. The effects of co-ion concentrations onto mono-component isotherm parameters (Langmuir and Freundlich) were studied and the inhibitory effect of co-ion concentration was observed. The effective reusability of biomass was assessed by three cycles of sorption-desorption. The sludge, owing to its high biosorption intensity and large availability from the local supply, is a better biosorbent for the treatment of Ni (II) and Cd (II) contaminated water.

INTRODUCTION

The growing population and industrial development pose a serious threat to water resources and ecosystems. One threat is the accretion of heavy metals, such as cadmium, mercury, nickel, lead, chromium, arsenic and their compounds. These are very toxic and some are subjected to bio-magnification (Orhan & Büyükgüngör 1993; Aksu & Dönmez 2006; Ahmaruzzaman 2011). Nickel and cadmium are of special interest since they are widely used together in many industries such as electroplating, smelting, alloy preparation, electronics, and battery manufacturing (Abu Al-Rub et al. 2003; Febrianto et al. 2009). The concentrations of these metals in the groundwater of certain areas of the state of Karnataka in India are high (KSPCB; Singh et al. 2010). According to the Central Pollution Control Board (India), the permissible discharge level of Ni (II) and Cd (II) with many of the industrial effluents into inland water is 3 mg/L and 2 mg/L respectively (CPCB).

The technology used in the removal of metal ions from wastewater in the process industries has evolved from conventional methods like chemical precipitation to adsorption processes using biosorbents. Recently, there has been a considerable amount of research regarding the use of low-cost industrial waste as biosorbents for detoxification of water contaminated with metal ions (Table 1). Microorganisms such as bacteria and yeast are used in breweries and food industries to aid fermentation. These industries are facing problems related to safe sludge disposal (Kuyucak 1990). In the current study, assessing the possible utilization of industrial waste brewery sludge, for the removal of Ni (II) and Cd (II) ions from aqueous solutions, has been explored. This study also addresses the effect of a co-ion presence during simultaneous biosorption of metal ions on the sludge.

METHODS

Preparation of biosorbent

Industrial waste sludge containing a yeast biomass of Saccharomyces carlsbergensis was obtained from United Breweries Limited, Nelamangala, India. The wet sludge was sun-dried for 72 h and later oven dried at 60 °C for 24 h. The dry sludge was powdered in a mortar and the yeast powder was sieved through 80–100 mesh to obtain an estimated average particle size of 150 μm.

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Key words | brewery sludge, cadmium and nickel ions, kinetics, preferential biosorption
Preparation of metal ion solution and metal ion analysis

Metal ion solutions of Ni (II) and Cd (II) of desired concentrations were prepared by suitably diluting the stock solutions. Stock solutions of 100 mg/L of Ni (II) and 100 mg/L of Cd (II) were prepared in 1,000 mL standard volumetric flasks by dissolving 0.4479 g of nickel sulphate \([\text{NiSO}_4\cdot6\text{H}_2\text{O}]\) and 0.2744 g of cadmium nitrate \([\text{Cd (NO}_3\text{)}_2\cdot4\text{H}_2\text{O}]\) in distilled water. For mixed metal studies, desired combinations of Ni (II) and Cd (II) were prepared by mixing suitable volumes of stock solutions of both metals. The initial pH of the metal solution was adjusted by using dilute sodium hydroxide or sulphuric acid solution.

The initial metal ion concentration and the residual concentration of Ni (II) and Cd (II) in the biosorption medium after biosorption was determined by atomic absorption spectrometer (GBC 932 plus) at a wavelength of 351.5 nm for Ni (II) and 326.1 nm for Cd (II). Before the analysis of residual metal ion concentrations, the samples were centrifuged, filtered using Whatman Grade 42 filter paper and the filtrate was analyzed using an atomic absorption spectrometer.

### RESULTS AND DISCUSSION

#### Effect of initial pH

As shown in Figure 1, barely any biosorption was seen at a pH of 2.0 as there was a high concentration of protons, which compete with metal ions for the binding sites of the sludge. The percentage of biosorption for Ni (II) increased from 1% to 35% when the pH of the solution was increased from 2.0 to 5.0. Similarly, in the case of the Cd (II) ion, the percentage of biosorption was found to have increased from 49% to 73%, at pH of 2.0 to 6.0. At higher pH, the metal ions became more competitive with hydrogen ions, resulting in an increased biosorption (Bermúdez et al. 2011; Amiri et al. 2014).

<table>
<thead>
<tr>
<th>Metal</th>
<th>Biomass type</th>
<th>Metal uptake (mg/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni (II)</td>
<td>Fly ash</td>
<td>0.03</td>
<td>Rao et al. (2002)</td>
</tr>
<tr>
<td></td>
<td>Baker’s yeast</td>
<td>11.40</td>
<td>Padmavathy et al. (2003)</td>
</tr>
<tr>
<td></td>
<td>Bagasse fly ash</td>
<td>1.12</td>
<td>Gupta et al. (2005)</td>
</tr>
<tr>
<td></td>
<td>Tea factory waste</td>
<td>15.26</td>
<td>Malkoc &amp; Nuhoglu (2005)</td>
</tr>
<tr>
<td></td>
<td>Activated sludge</td>
<td>4.06</td>
<td>Ajaykumar et al. (2009)</td>
</tr>
<tr>
<td></td>
<td>Brewer’s yeast</td>
<td>5.34</td>
<td>Cui et al. (2010)</td>
</tr>
<tr>
<td></td>
<td>Sugarcane bagasse</td>
<td>2.00</td>
<td>Alomí et al. (2012)</td>
</tr>
<tr>
<td></td>
<td>\textit{Saccharomyces cerevisiae}</td>
<td>1.57</td>
<td>Galedar &amp; Younesi (2013)</td>
</tr>
<tr>
<td></td>
<td>Nanocellulose fibers of rice straw</td>
<td>8.55</td>
<td>Kardam et al. (2014)</td>
</tr>
<tr>
<td></td>
<td>\textit{Elaeagnus angustifolia}</td>
<td>2.42</td>
<td>Present study</td>
</tr>
<tr>
<td>Brewery sludge</td>
<td>7.87</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cd (II)</td>
<td>\textit{Aspergillus niger}</td>
<td>4.0</td>
<td>Kapoor &amp; Viraraghavan (1998)</td>
</tr>
<tr>
<td></td>
<td>Bagasse fly ash</td>
<td>1.24</td>
<td>Gupta et al. (2005)</td>
</tr>
<tr>
<td></td>
<td>Activated sludge</td>
<td>18.08</td>
<td>Ajaykumar et al. (2009)</td>
</tr>
<tr>
<td></td>
<td>Brewer’s yeast</td>
<td>10.17</td>
<td>Cui et al. (2010)</td>
</tr>
<tr>
<td></td>
<td>\textit{Aspergillus aculeatus}</td>
<td>14.24</td>
<td>Panday &amp; Banerjee (2012)</td>
</tr>
<tr>
<td></td>
<td>Baker’s yeast</td>
<td>2.36</td>
<td>Wang (2012)</td>
</tr>
<tr>
<td></td>
<td>\textit{Saccharomyces cerevisiae}</td>
<td>3.74</td>
<td>Galedar &amp; Younesi (2013)</td>
</tr>
<tr>
<td></td>
<td>Nanocellulose fibers of rice straw</td>
<td>9.7</td>
<td>Kardam et al. (2014)</td>
</tr>
<tr>
<td></td>
<td>\textit{Elaeagnus angustifolia}</td>
<td>1.97</td>
<td>Amiri et al. (2014)</td>
</tr>
<tr>
<td>Brewery sludge</td>
<td>13.96</td>
<td>Present study</td>
<td></td>
</tr>
</tbody>
</table>

**Table 1** Biosorption capacity of different low cost and industrial waste biosorbents for Ni (II) and Cd (II) removal

- **Preparation of metal ion solution and metal ion analysis**
- **RESULTS AND DISCUSSION**
- **Effect of initial pH**

**Batch biosorption experiments**

The biosorption process was studied through batch experiments, to examine the influence of different factors such as initial pH (2.0–9.0), contact time (10–180 min), sludge dosage (2–40 g/L), initial metal ion concentration (10–50 mg/L), temperature (30–50 °C) and co-ion concentrations on biosorption of Ni (II) and Cd (II) on the sludge. The batch experiments were performed in 250 mL Erlenmeyer flasks with a working volume of 50 mL in an incubator orbital shaker at 150 rpm. All the experiments were conducted in duplicate and the mean values were shown in the results. Error bars are provided in all the related figures.

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Metal ion solutions of Ni (II) and Cd (II) of desired concentrations were prepared by suitably diluting the stock solutions. Stock solutions of 100 mg/L of Ni (II) and 100 mg/L of Cd (II) were prepared in 1,000 mL standard volumetric flasks by dissolving 0.4479 g of nickel sulphate \([\text{NiSO}_4\cdot6\text{H}_2\text{O}]\) and 0.2744 g of cadmium nitrate \([\text{Cd (NO}_3\text{)}_2\cdot4\text{H}_2\text{O}]\) in distilled water. For mixed metal studies, desired combinations of Ni (II) and Cd (II) were prepared by mixing suitable volumes of stock solutions of both metals. The initial pH of the metal solution was adjusted by using dilute sodium hydroxide or sulphuric acid solution.

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The negative charge of the functional groups on the sludge promoted biosorption with metal cations. In an alkaline condition, formation of metal hydroxide complex inhibits the contact of metal ions to the biomass. The maximum biosorption of Ni (II) and Cd (II) on the yeast biomass was observed at a pH of 5.0 for Ni (II) and at pH 6.0 for Cd (II).

Effect of contact time and biosorption kinetics

As shown in Figure 2, the maximum removal rate for Ni (II) was 35% and 73% for Cd (II) at 120 min when equilibrium was achieved. The applicability of the pseudo-first order (Equation (1)) and pseudo-second order kinetic models (Equation (2)) were tested using the data shown in Figure 2.

\[
\log (q_e - q) = \log q_e - \left( \frac{k_1}{2.303} \right) t
\]

\[
\frac{t}{q} = \frac{1}{k_2 q_e} + \frac{t}{q_e}
\]

where, \(q\) and \(q_e\) are metal uptake (mg/g) at time \(t\) and at equilibrium time, \(k_1\) is the pseudo-first order rate constant (min\(^{-1}\)), \(t\) is the contact time (min), and \(k_2\) is the pseudo-second order rate constant (g mg\(^{-1}\) min\(^{-1}\)).

The calculated model parameters are presented in Table 2. Ni (II) and Cd (II) biosorption onto the sludge follows a pseudo-second order kinetic model \((R^2 \approx 0.99)\) but not a pseudo-first order model. This indicates that the surface reaction through sharing or exchange of ions is the rate controlling step for biosorption of Ni (II) and Cd (II) ions by the sludge (Ho & McKay 1999; Alomá et al. 2012).

Effect of sludge dosage

The increase in the sludge dosage increases the number of binding sites for biosorption. It is seen from Figure 3 that as the sludge dosage increased from 2 g/L to 40 g/L, the percentage biosorption was found to increase from 26% to 39% for Ni (II) and 66% to 79% for Cd (II). The dosage effect (2–40 g/L) is similar for both Ni (II) and Cd (II) biosorption, with a total increase in the removal rate of around 13%. The increase in the sludge dosage can be attributed to an increase in the active biosorbent sites (Akar et al. 2009; Kulkarni et al. 2018).

Table 2 | Pseudo-first order and pseudo-second order kinetic parameters for Ni (II) and Cd (II) biosorption on the sludge with goodness of fit of model

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>Experimental (q_e) (mg/g)</th>
<th>Predicted (q_e) (mg/g)</th>
<th>(k_1) (min(^{-1}))</th>
<th>(R^2)</th>
<th>Predicted (q_e) (mg/g)</th>
<th>(k_2) (g/mg.min)</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni (II)</td>
<td>4.37</td>
<td>2.28</td>
<td>0.026</td>
<td>0.8493</td>
<td>4.95</td>
<td>0.005</td>
<td>0.991</td>
</tr>
<tr>
<td>Cd (II)</td>
<td>9.07</td>
<td>0.31</td>
<td>0.029</td>
<td>0.7155</td>
<td>9.10</td>
<td>0.111</td>
<td>0.999</td>
</tr>
</tbody>
</table>
Effect of initial Ni (II) and Cd (II) metal ion concentration and temperature

The percentage biosorption decreased from 49% to 35% at 30 °C, 41% to 31% at 40 °C and 33% to 23% at 50 °C, with an increase in Ni (II) ion concentration from 10 mg/L to 50 mg/L (Figure 4). Similarly, the percentage biosorption decreased from 86% to 73% at 30 °C, 81% to 65% at 40 °C and 74% to 54% at 50 °C with an increase in Cd (II) ion concentration from 10 mg/L to 50 mg/L (Figure 5). The decrease in biosorption is due to the increased number of metal ions competing for the available active sites on the sludge (Guyo et al. 2016). It is evident from Figures 4 and 5 that the biosorption of Ni (II) and Cd (II) ions onto the sludge is controlled by an exothermic process. The maximum uptake occurred at 30 °C in the selected temperature range of 30 °C to 50 °C.

Isotherms for single metal biosorption

The Langmuir and Freundlich models were used to describe the equilibrium biosorption data (Table 3). The linearized form of the Langmuir isotherm (Equations (3) and (4)) and the Freundlich isotherm (Equation (5)) are

\[
\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{q_{max}bC_e} \tag{3}
\]

\[
R_L = \frac{1}{1 + bC_0} \tag{4}
\]

\[
\ln q_e = \frac{1}{n} \ln C_e + \ln K \tag{5}
\]

where \(q_{max}\) is the maximum monolayer biosorption capacity of the biosorbent (mg/g), \(b\) is biosorption affinity in L/mg, \(K\) and \(n\) are equilibrium constants indicative of biosorption capacity (mg g\(^{-1}\) L mg\(^{-1}\)\(1/2\)) and biosorption affinity respectively, \(R_L\) is the Hall separation factor, \(C_0\) is the initial metal ion concentration in mg/L.

The values of the coefficient of determination being near to one (>0.97) suggest that both models provide a good fit to the equilibrium biosorption data at all the studied temperatures. Table 1 provides a summary of the sludge biosorption capacity compared with the different low cost and industrial waste biosorbents for Ni (II) and Cd (II) removal. It is clearly evident from the comparison that the maximum biosorption capacity of the sludge is fairly high compared to some of the reported biosorbents.

Effect of co-ions in biosorption of nickel (II) and cadmium (II)

Biosorption of Ni (II) and Cd (II) ions from the binary solutions of metal ions on the sludge was examined and
Table 3 | Langmuir and Freundlich isotherm parameters for Ni (II) and Cd (II) biosorption on brewery sludge

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>Temperature (°C)</th>
<th>Langmuir isotherm</th>
<th>Freundlich isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>q&lt;sub&gt;max&lt;/sub&gt; (mg/g)</td>
<td>b (L/mg)</td>
</tr>
<tr>
<td>Ni (II)</td>
<td>30</td>
<td>7.874</td>
<td>35.45 × 10&lt;sup&gt;-3&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>7.092</td>
<td>28.67 × 10&lt;sup&gt;-3&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>6.514</td>
<td>22.17 × 10&lt;sup&gt;-3&lt;/sup&gt;</td>
</tr>
<tr>
<td>Cd (II)</td>
<td>30</td>
<td>13.966</td>
<td>12.53 × 10&lt;sup&gt;-2&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>12.886</td>
<td>10.04 × 10&lt;sup&gt;-2&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>10.193</td>
<td>8.64 × 10&lt;sup&gt;-2&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

Biosorption isotherms – effect of co-ion on mono component isotherm parameters

Biosorption isotherms for the biosorption of Ni (II) and Cd (II) on the sludge were analyzed in both single and binary metal solutions to study the effect of co-ion concentrations on the mono-component isotherm parameters (Table 4). This helps in studying the alteration of equilibrium in the presence of co-ions. The values of the Langmuir and Freundlich constants, q<sub>max</sub> and K were found to decrease with an increase in co-ion concentrations. The b and n values obtained were found to be higher for Cd (II) than for Ni (II), indicating a higher affinity of the sludge toward Cd (II). The sequence of selectivity followed the order of decreasing electronegativity, increasing ionic radius and atomic weight and decreasing hardness (Aksu & Dönmez 2006; Kulkarni et al. 2014). Cd (II) will be preferentially biosorbed over Ni (II) due to greater affinity for the carboxylic groups existing on the sludge (Abu Al-Rub et al. 2003; Kleinübing et al. 2011). It was observed that the biosorption capacity of the sludge in the dual metal system was lower than the single metal ion system.

Characterization of biomass

The surface images of the sludge before and after Ni (II) and Cd (II) biosorption (Figure S1) were obtained using a scanning electron microscope (JEOL, Japan) with energy dispersive X-ray spectroscopy (EDX). The biosorbent surface was observed to be rough before biosorption. Biosorption of metal ions has led to the formation of aggregates on the sludge surface, which may be due to complexation of metal ions with the cell surface. EDX analysis showed the presence of Ni (II) and the presence of Cd (II) on the biomass surface along with other components of the biomass sample (C,N,O,P,S) after Ni (II) and Cd (II) biosorption.

Infrared spectra of biosORBents loaded with and without metal ions were recorded using a Fourier transform-infrared (FTIR) spectrometer (Bruker alpha) in the range of 4,000–500 cm<sup>-1</sup>, with a resolution of 4 cm<sup>-1</sup> (Figure S2). After nickel biosorption, the band at 2,919.7 cm<sup>-1</sup> shifts to 2,925.6 cm<sup>-1</sup>, 1,641.5 cm<sup>-1</sup> to 1,638.5 cm<sup>-1</sup>, 1,532.6 cm<sup>-1</sup> to 1,535.5 cm<sup>-1</sup> and 1,037.3 cm<sup>-1</sup> to 1,039.7 cm<sup>-1</sup>. Similar observations were made with the FTIR spectra of the sludge after Cd (II) biosorption with a band shift from 2,919.7 cm<sup>-1</sup> to 2,923.6 cm<sup>-1</sup>, 1,641.5 cm<sup>-1</sup> to 1,637 cm<sup>-1</sup>, 1,532.6 cm<sup>-1</sup> to 1,531.5 cm<sup>-1</sup> and 1,037.3 cm<sup>-1</sup> to 1,034.6 cm<sup>-1</sup>, which indicates that the –CH<sub>2</sub>–, –OH, –C = O, –NH<sub>2</sub> and C-O anionic functional groups present on the sludge are involved in the biosorption.
Desorption, regeneration and reuse studies

The application of biosorbent towards detoxification of metal bearing effluents depends not only on its biosorption capacity, but also on how well the metal may be recovered from the biosorbent surface; the possibility of biomass regeneration and reuse. The metal loaded biomass, after adsorption was contacted with 50 mL of 0.1N HCl eluant to study desorption of metal ions (Table S3).

The reusability of the sludge was evaluated in three consecutive cycles of biosorption-desorption using HCl eluant and regeneration using distilled water in a batch system. Acid treatment with 0.1 M HCl was found to be the most effective, where more than 90% of metal was desorbed from the spent sludge throughout the three cycles. Only 12.7% decrease in sorption of Ni (II) and 5.62% decrease in sorption of Cd (II) by the biomass were observed in three cycles, indicating effectiveness of the desorption–regeneration process (Table S4).

CONCLUSIONS

This study identified brewery sludge as a suitable biosorbent to be utilized for treating Ni (II) and Cd (II) ions from metal contaminated water. The optimal biosorption conditions for the selected metal removal were determined using the batch mode of studies. The biosorption mechanism followed the pseudo-second order kinetic model. Preferential biosorption of Cd (II) over Ni (II) was observed in both cases of single and dual metal ion biosorption on to the sludge. The metal uptake was found to decrease with increase in co-ion concentration, indicating competitive biosorption and interference of co-ions during biosorption. Brewery sludge possesses advantages such as abundant availability, good biosorption capacity and intensity and ease of regeneration with possibilities of metal recovery. This makes biosorption by the sludge an attractive treatment option for Ni (II) and Cd (II) bearing water.

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CONFLICT OF INTEREST

The authors have declared no conflict of interest.

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KS PCB. Karnataka State Pollution Control Board. http://kspcb.kar.nic.in/annual_reports.html.


